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LXV.—ON SOME NITRO DERIVATIVES OF METABROMTOLUOL.

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Determination of the Constitution of Metabromdinitrotoluol, $C_6H_2CH_3Br(NO_2)_2$.

Our attention was first called to this subject by Prof. C. Loring Jackson, who, having with W. S. Robinson[2] obtained the metabromdinitrotoluol by the decomposition of their bromdinitrophenylmalonic ester, asked us to determine its constitution.

This metabromdinitrotoluol, melting point 103°–104°, was discovered by Grete,[3] who made it by the action of fuming nitric acid on metabromtoluol, or metabrommononitrotoluol, and assigned to it the constitution CH_3, NO_2, Br, NO_2, 1, 2, 3, 4, although he was very doubtful about the position of the second nitro group, giving it the para position without any experimental reason for doing so. His proof that one of the nitro groups was in the ortho position consisted in establishing the identity of the bromtoluidine made by the reduction of his bromnitrotoluol with that obtained by the action of bromine on orthoacettoluid;[4] but this obviously leaves it

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] This Journal **11**. [3] Ann. Chem. (Liebig) **168**, 258.

[4] Wroblewsky, Ann. Chem. (Liebig) **168**, 161.

doubtful whether this nitro group stands in the position 2 or 6 to the methyl of the toluol, and in fact later work has shown that Grete was wrong in ascribing to it the position 2, as his mononitro compound really has the constitution CH_3, Br, NO_2, 1, 3, 6. The proof of this was given by Nevile and Winther,[1] who, by replacing the amido group in the metabromorthotoluidine (melting point 55°–56°) already mentioned by bromine, obtained a liquid dibromtoluol, which on oxidation with nitric acid yielded the dibrombenzoic acid melting at 151°–153° previously made by Von Richter[2] from paradibrombenzol.

The only point therefore not settled in regard to the constitution of Grete's metabromdinitrotoluol was the position of the second nitro group, which might be either para or ortho to the methyl. To determine this the metabromdinitrotoluol was heated with alcoholic ammonia[3] in sealed tubes to 100° for twelve hours, when it was found to be converted into a yellow substance, which had partly separated in the solid state, and partly remained in solution in the alcohol, from which it was obtained by evaporation. The product was purified by washing with water to remove the ammonic bromide, and crystallisation from hot glacial acetic acid, until it showed a constant melting point (193°–194°), when it was dried at 135°, and the following analysis showed that a dinitrometatoluidine had been formed.

0.2658 gram of the substance gave 51.2 cc. of nitrogen at a temperature of 24° and a pressure of 767.5 mm.

	Calculated for $C_6H_2CH_3NH_2(NO_2)_2$.	Found.
Nitrogen	21.31	21.71

The melting point showed that this substance is identical with the dinitrotoluidine made by Hepp[4] by the action of alcoholic ammonia on his γ trinitrotoluol, but the constitution of this trinitrotoluol had not been determined. Staedel[5] has also announced recently that one of his students, Herr Adalbert Kolb, has prepared a dinitrotoluidine from dinitrokresolether and determined its constitution as CH_3, NH_2, NO_2, NO_2, 1, 3, 4, 6; but, as he neglected to give the melting point, we were unable to tell whether it was identical with ours or not, and have been forced to work

[1] Ber. d. chem. Gesell. **13**, 962. [2] Ibid. **7**, 1146.

[3] When metabromdinitrotoluol was allowed to stand with alcoholic ammonia in the cold, a dark blue solution was formed at first, but the color gradually changed to reddish brown.

[4] Ann. Chem. (Liebig) **215**, 371. [5] Ber. d. chem. Gesell. **22**, 215.

out the constitution of our dinitrotoluidine by the replacement of the amido group by hydrogen. In doing this some difficulty was encountered because of the very slight solubility of the dinitrotoluidine in alcohol, but we found on experiment that the Griess reaction would take place satisfactorily in a mixture of acetone and alcohol, and accordingly proceeded as follows: 2 grams of the dinitrotoluidine were dissolved in about 12 cc. of acetone, 8 cc. of common alcohol added, and the mixture acidified with strong sulphuric acid, after which 1.5 grams of sodic nitrite, about twice the calculated amount, was added in small portions at a time, and the liquid warmed gently until the evolution of nitrogen ceased, when the larger part of the acetone and alcohol was distilled off at first on the water-bath, finally on the sand-bath, and the residue distilled with steam; the dinitrotoluol passed over into the receiver in small white crystals, which were removed by filtration, and crystallised from hot alcohol until they showed the constant melting point 71°. It was not worth while to dilute the distillate of acetone and alcohol, as no precipitate was obtained in that way. For greater certainty the product was analysed, with the following results:

0.2456 gram of the substance gave 33.1 cc. of nitrogen at a temperature of 22° and a pressure of 764.2 mm.

	Calculated for $C_6H_3CH_3(NO_2)_2$.	Found.
Nitrogen	15.38	15.29

There is no question, therefore, that the substance is the ortho-paradinitrotoluol, CH_3, NO_2, NO_2, 1, 2, 4, and the bromdinitrotoluol accordingly has the following constitution: CH_3, Br, NO_2, NO_2, 1, 3, 4, 6. It follows also that our dinitrotoluidine is identical with that described by Kolb, and, if Staedel had given its melting point, it would not have been necessary for us to determine its constitution. As has been already stated, this dinitrotoluidine melts at the same point as that made by Hepp from alcoholic ammonia and his γ trinitrotoluol. To establish the relation between these substances more firmly, we made the dinitrophenyltoluidine by treating our dinitrobromtoluol with aniline, and found that the product showed the same melting point, 142°, as that of the compound made by Hepp from γ trinitrotoluol and aniline. The γ trinitrotoluol of Hepp, therefore, has the following constitution: CH_3, NO_2, NO_2, NO_2, 1, 3, 4, 6; which is in harmony

with Laubenheimer's rule,[1] that a nitro group is removed by the action of alcoholic ammonia only when it is in the ortho position to another nitro group.

Metabromtrinitrotoluol, $C_6HCH_3Br(NO_2)_3$.

In preparing the metabromdinitrotoluol we found, if a mixture of fuming nitric acid and sulphuric acid was used, that a new substance melting above 104° was obtained, which turned out to be the as yet undescribed metabromtrinitrotoluol. This compound is most easily prepared from the metabromdinitrotoluol, when it is convenient to proceed as follows: 5 to 10 grams of metabromdinitrotoluol were placed in a flask, and 10 to 20 cc. of a mixture of two volumes of fuming nitric acid and one of strong sulphuric acid added. The whole was then boiled until the evolution of red fumes had nearly ceased, when, after it was cool, it was poured in a fine stream into a beaker of cold water, stirring the liquid vigorously during the addition of the acid solution, as in this way the product is precipitated in a granular form much more easy to manage than the large compact lumps obtained if the stirring is neglected. The product was then washed with cold water till free from acid, and purified by crystallisation from alcohol, until it showed the constant melting point 143°. The residue from the mother liquors, consisting of a mixture of metabromtrinitrotoluol and the corresponding dinitro compound, can be advantageously used for preparing a fresh quantity of the trinitro body. The pure substance was dried at 120°, and analysed with the following results:

I. 0.3372 gram of the substance gave on combustion 0.3356 gram of carbonic dioxide and 0.0453 gram of water.

II. 0.2651 gram of the substance gave 32.9 cc. of nitrogen at a temperature of 21° and a pressure of 761.5 mm.

III. 0.1830 gram of the substance gave, by the method of Carius, 0.1120 gram of argentic bromide.

	Calculated for $C_6HCH_3Br(NO_2)_3$.	Found. I.	II.	III.
Carbon	27.46	27.14	...	...
Hydrogen	1.31	1.49	...	...
Nitrogen	26.14	...	26.04	...
Bromine	13.73	...	...	14.09

The yield was about 60 per cent. of the theoretical.

[1] Ber. d. chem. Gesell. **9**, 766, 1828.

Properties.—The metabromtrinitrotoluol crystallises from alcohol in small white needles, which melt at 143°. They are insoluble in water or ligroin; nearly insoluble in cold alcohol, only sparingly soluble in hot; slightly soluble in carbonic disulphide; soluble in ether, methyl alcohol, benzol, chloroform, glacial acetic acid, or acetone. Boiling alcohol we found the best solvent for it, although it is so slightly soluble in it. Aqueous sodic hydrate seemed to have no action upon it, nor was it affected by the strong acids. The bromine is removed easily, which we proved by the action of alcoholic ammonia or aniline on it, as will be described later in this paper.

Constitution of Metabromtrinitrotoluol.

As the metabromtrinitrotoluol is made from the metabromdinitrotoluol, the only point to be determined is the position of the third nitro group; for this purpose we converted it into the corresponding trinitrotoluidine by treatment with alcoholic ammonia in the cold. The mixture was allowed to stand in a corked flask for about twelve hours; at first a dark blue color appeared in the liquid, but on longer standing this turned to a deep reddish brown, and a precipitate was deposited, which with the supernatant liquid at the end of the twelve hours was poured into a dish and the solvent allowed to evaporate spontaneously. The residue, which was red and yellow, was washed till free from ammonic bromide, and then purified by crystallisation from hot glacial acetic acid, until it showed the constant melting point 136°, when it was dried at 120° and analysed with the following result:

0.1144 gram of the substance gave 24.2 cc. of nitrogen at a temperature of 23° and a pressure of 754.7 mm.

	Calculated for $C_6HCH_3NH_2(NO_2)_3$.	Found.
Nitrogen	23.14	23.51

The melting point of this trinitrotoluidine shows that it is identical with that prepared by Nölting and Salis[1] by the action of alcoholic ammonia on trinitrometakresolethylether, to which they assign the constitution CH_3, NO_2, NH_2, NO_2, NO_2, 1, 2, 3, 4, 6, on the ground that the alcoholic ammonia did not remove any of the nitro groups, and therefore, according to Laubenheimer,[2] no two of them could be in the ortho position to each other, and this is the only possible arrangement in which no two nitro groups are

[1] Ber. d. chem. Gesell. **15**, 1864. [2] Ibid. **9**, 766, 1828.

in the ortho position. Our metabromtrinitrotoluol must consequently have the constitution CH_3, NO_2, Br, NO_2, NO_2, 1, 2, 3, 4, 6; and this conclusion is confirmed by the fact recently discovered in this laboratory,[1] that the bromtrinitrophenylmalonic ester is converted by boiling with sulphuric acid of specific gravity 1.44 into this metabromtrinitrotoluol melting at 143°. As the bromtrinitrophenylmalonic ester is made from the symmetrical tribromtrinitrobenzol, Br, NO_2, Br, NO_2, Br, NO_2, 1, 2, 3, 4, 5, 6, it can have only the constitution $CH(COOC_2H_5)_2$, NO_2, Br, NO_2, NO_2, 1, 2, 3, 4, 6, which leads to the constitution of our metabromtrinitrotoluol given above.

Anilidotrinitrotoluol, $C_6HCH_3(C_6H_5NH)(NO_2)_2$.

This substance was prepared by treating metabromtrinitrotoluol with aniline in the proportion of two molecules of the base to one of the nitro compound; the action is violent, accompanied with considerable evolution of heat, and the product was easily purified by crystallisation from a mixture of alcohol and benzol, until it showed the constant melting point 151°, when it was dried at 120°, and analysed with the following results:

I. 0.2804 gram of the substance gave on combustion 0.5031 gram of carbonic dioxide and 0.0936 gram of water.

II. 0.2777 gram of the substance gave 43.2 cc. of nitrogen at a temperature of 27.5° and a pressure of 772 mm.

	Calculated for $C_6HCH_3(C_6H_5NH)(NO_2)_2$.	Found. I.	II.
Carbon	49.06	49.03	...
Hydrogen	3.14	3.71	...
Nitrogen	17.61	...	17.41

Properties.—The metanilidotrinitrotoluol crystallises from a mixture of alcohol and benzol in well developed shining yellow plates, which melt at 151°. The substance is insoluble in water or ligroin; sparingly soluble in ethyl or methyl alcohol; soluble in ether, chloroform, benzol, carbonic disulphide, glacial acetic acid, or acetone. The most convenient solvent for it is a mixture of five parts of alcohol with one of benzol. Aqueous sodic hydrate dissolves it with a red color, and hydrochloric acid throws down from this solution the original substance apparently unaltered.

[1] See next paper, page 19.

Strong sulphuric or strong nitric acid dissolves it, but strong hydrochloric acid does not.

The constitution of this substance is CH_2, NO_2, C_6H_3NH, NO_2, NO_2, 1, 2, 3, 4, 6, as is shown by its preparation from the metabromtrinitrotoluol, the constitution of which has been determined, as given earlier in this paper.

LXVI.—ON THE ACTION OF SODIUM MALONIC ESTER UPON TRIBROMTRINITROBENZOL.

By C. Loring Jackson and George Dunning Moore.[1]

In a previous paper[2] one of us with J. F. Wing described the preparation of tribromtrinitrobenzol, and announced that its action with sodium malonic ester would be studied. This work promised to be of especial interest, because we hoped that each of the bromine atoms would be replaced by the radical $CH(COOC_2H_5)_2$, and that by the reduction of the substance thus formed a compound might be obtained consisting of three pyrrol molecules united to form a central benzol ring, a sort of triple indol. Our first experiments, however, showed that the reaction did not run in the way we had expected, but instead of the removal of all three of the bromine atoms only two were replaced, one by the radical $CH(COOC_2H_5)_2$, the other by hydrogen giving a product with the following formula,

$$C_6HBr(NO_2)_3CH(COOC_2H_5)_2,$$

that is, bromtrinitrophenylmalonic ester. After we had established the composition of this substance, we decided that it was unwise to undertake a complete study of this trinitro compound, which can be obtained only with a very considerable outlay of time and material, when the corresponding dinitro compound can be made much more easily, and resembles it closely in most respects. We have accordingly confined our work principally to those properties of the trinitro compound in which we have observed marked differences from the corresponding ones of the dinitro body, and for a fuller discussion of those properties which the two substances

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] This Journal **10**, 283 (1888).

have in common would refer the reader to a paper "On the Action of Sodium Malonic Ester on Tribromdinitrobenzol" by one of us and W. S. Robinson.[1]

The results described in this paper can be briefly stated as follows. Sodium malonic ester forms in the cold with tribromtrinitrobenzol bromtrinitrophenylmalonic ester,

$$C_6HBr(NO_2)_2CH(COOC_2H_5)_2, \text{ melting point } 104°\text{–}105°,$$

which has acid properties forming salts even with aqueous solutions of the alkaline carbonates. Of these the red soluble sodium salt has been studied, and its analysis led to the formula

$$C_6HBr(NO_2)_2CNa(COOC_2H_5)_2.$$

The yellow insoluble copper salt, on the other hand, gave no constant result on analysis, but on several occasions, in trying to make it from a solution of cupric chloride in alcohol and the sodium salt, a crystalline substance free from copper was obtained melting in the neighborhood of 75°. Unfortunately the end of the term has prevented us from studying this substance, which is the more interesting because no similar compound has been obtained from the corresponding dinitro body.

The reactions by which the bromtrinitrophenylmalonic ester is derived from tribromtrinitrobenzol have been made out as follows:

$$C_6Br_3(NO_2)_3 + 3CHNa(COOC_2H_5)_2 =$$
$$NaBr + C_6Br_2(NO_2)_3CH(COOC_2H_5)_2 + 2CHNa(COOC_2H_5)_2 =$$
$$C_6Br_2(NO_2)_3CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2$$
$$+ CHNa(COOC_2H_5)_2 + NaBr =$$
$$C_6HBr(NO_2)_3CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2$$
$$+ CHNa(COOC_2H_5)_2 + NaBr =$$
$$C_6HBr(NO_2)_3CNa(COOC_2H_5)_2 + 2NaBr + C_2H_2(COOC_2H_5)_4.$$

The acetylentetracarbonic ester formed according to the last reaction was obtained from the oily secondary product of the action by distillation under diminished pressure, and identified by its melting point and analysis.

Perhaps the most striking difference between the dinitro and trinitro compounds consisted in the fact that the trinitro ester, or its salts, when heated with an excess of common strong nitric acid, turned bright blood-red, whereas no such action could be obtained from the dinitro compound. The red product, on crystallisation

[1] This Journal **11**, 93 (1889).

from alcohol, was converted into colorless crystals melting at 215°, and as they melted becoming blood-red and increasing very much in volume. The study of this curious substance is still unfinished; we have only established the fact that it is an ester. If the action of the nitric acid is long continued, another body is formed melting at 156° to a colorless liquid, and dissolving in aqueous sodic hydrate with a red color.

Sulphuric acid of specific gravity 1.44 converts the ester into the metabromtrinitrotoluol melting at 143°–144°, recently discovered in this laboratory by Bentley and Warren.

The trinitrophenylendimalonic ester (melting point 123°),

$$C_6H(NO_2)_3[CH(COOC_2H_5)_2]_2,$$

was also obtained by the further action of sodium malonic ester on bromtrinitrophenylmalonic ester; strangely enough, it has less marked acid properties than the bromine compound, from which it is derived.

Preparation of Bromtrinitrophenylmalonic Ester.

The tribromtrinitrobenzol used for this purpose was prepared according to the method already given by one of us and J. F. Wing;[1] we have found, however, that if the proportion of fuming sulphuric acid is increased, a better yield is obtained. The proportions finally used were 20 grams of tribromdinitrobenzol, 500 cc. of the nitric acid of 1.52 specific gravity, and 200 cc. of fuming sulphuric acid, instead of one-third the volume of the nitric acid as previously recommended. The yield obtained from the new proportions was in the neighborhood of 40 per cent. of the theory, running in one case as high as 45 per cent., whereas the proportions recommended by one of us and Wing gave on the average from 15 to 20 per cent., and only in a single instance ran as high as 40 per cent.

To convert the tribromtrinitrobenzol into bromtrinitrophenylmalonic ester, one molecule of it must be treated with about three molecules of sodium malonic ester. In practice we found it convenient to proceed as follows: 10 grams of tribromtrinitrobenzol were dissolved in about 100 cc. of benzol with the aid of heat, mixed, while the solution was still moderately warm, with 10.6 grams of malonic ester previously converted into the sodium com-

[1] This Journal **10**, 284 (1888).

pound by treatment with the sodic ethylate from 1.7 grams of sodium (a slight excess over the calculated amount) and about 75 cc. of absolute alcohol, and the mixture allowed to stand 40 to 60 hours in a corked flask at ordinary temperatures. As soon as the sodium malonic ester was added the liquid became dark blood-red, and on standing this color gradually increased in intensity, while at the same time a precipitate of sodic bromide was thrown down. The product of the reaction was mixed with about three-quarters of a liter of water, and acidified with dilute sulphuric acid,[1] which decomposed the red salt, setting free the ester. Ether was then added, and, after shaking thoroughly, the ethereal and benzol solution separated from the aqueous liquid, which was extracted once more with ether. On distilling off the ether and benzol from the extract, a dark oily residue was left, which was mixed with a little alcohol, when, upon stirring, it solidified to a mass of prismatic crystals. These were sucked out on the pump, washed with a little cold alcohol to remove the adhering oil, and purified by crystallisation from hot alcohol, till they showed the constant melting point 104°–105°. The oil which was sucked out from the crystals, or removed from them by alcohol, upon standing, deposited an additional amount of the substance, which was purified in the same way as the main portion. The substance, after being dried *in vacuo*, was analysed with the following results:

I. 0.2235 gram of the substance gave on combustion 0.2860 gram of carbonic dioxide and 0.0629 gram of water.

II. 0.1930 gram of the substance gave 16.2 cc. of nitrogen at a temperature of 21° and under a pressure of 775.9 mm.

III. 0.2548 gram gave 20.1 cc. of nitrogen at 18.5° and 784 mm. pressure.

IV. 0.2080 gram gave by the method of Carius 0.0870 gram of argentic bromide.

V. 0.2512 gram gave 0.1034 gram of argentic bromide.

	Calculated for $C_6HBr(NO_2)_2CH(COOC_2H_5)_2$.	Found.				
		I.	II.	III.	IV.	V.
Carbon	34.67	34.89	...	...	...	...
Hydrogen	2.67	3.13	...	...	...	...
Nitrogen	9.33	...	9.75	9.38	...	...
Bromine	17.78	...	...	...	17.80	17.52

[1] Dilute nitric acid, which was used in some of the earlier preparations, seemed to diminish the yield.

The yield was good, when compared to that obtained in similar preparations from other substances; the best result was as follows: 10 grams of tribromtrinitrobenzol, treated as described above with 10.6 grams of malonic ester, gave 6.4 grams of bromtrinitrophenylmalonic ester. The amount required by theory, if all the tribromtrinitrobenzol had been converted into bromtrinitrophenylmalonic ester, is 10 grams; therefore the yield is 64 per cent. of the theoretical. The average yield was between 50 and 60 per cent. of the theoretical.

Properties.—The bromtrinitrophenylmalonic ester crystallises in white slender needles arranged in radiating groups, which, when examined with the microscope, are seen to be flat needles, or long plates terminated by one plane, or, as commonly, by two at an obtuse angle to each other. The crystals seem to belong to the monoclinic system. The melting point is 104°–105°, and if heated to 160° the substance becomes dark red and gives off gas. It is essentially insoluble in cold water, very slightly soluble in hot; insoluble in ligroin; slightly soluble in ether; not very soluble in cold, freely in hot ethyl or methyl alcohol; freely in benzol, carbonic disulphide, or glacial acetic acid; very freely in chloroform or acetone. Hot alcohol is the best solvent for it. Strong hydrochloric acid has no action upon it, even when the substances are warmed together in open vessels; it is probable, however, that in sealed tubes the same decomposition would take place as that observed with the corresponding dinitro body. Strong sulphuric acid dissolves a little in the cold, more when hot, forming a colorless solution. Strong nitric acid has little or no action in the cold, but, if warmed with it, converts it into an intensely red viscous substance swimming in the red acid liquid, which by further action of strong nitric acid becomes solid and crystalline. A fuller discussion of the action of strong nitric acid and that of dilute sulphuric acid will be found later in this paper.

As was to be expected from the position of one of its hydrogen atoms on a carbon surrounded by two carboxylester radicals and a trinitrophenyl group, the substance possesses marked acid properties. Sodic hydrate in excess gives only a pale red color with the solid ester, owing to the very slight solubility of the sodium salt in sodic hydrate, but upon adding water the coloration increases, and the addition of a few drops of alcohol produces a very dark red solution. Potassic carbonate in aqueous solution gives a slight red color, on the addition of a little alcohol a dark

red solution; acid sodic carbonate acts in much the same way, but the color produced by the aqueous solution is paler than that given with potassic carbonate. Ammonic hydrate gives a red color at once, but this cannot be obtained free from ammonia by evaporation on the water-bath or by using an excess of the ester. The behavior of such a solution made by using an excess of the ester with ammonic hydrate was studied nevertheless, and the following are the more characteristic precipitates which were obtained:

Magnesium salt, pale rust-colored.

Calcium salt, pale red flocks.

Strontium salt, like that obtained from calcium, but not so heavy a precipitate.

Barium salt, an even less heavy precipitate than that obtained with strontium, also less flocculent.

Manganese salt, yellowish brown.

Zinc salt, pale red.

Cobalt or Nickel salts, yellowish.

Ferric salt, rust-colored.

Cupric salt, a rusty red to orange.

Mercuric chloride, yellowish brown.

Mercuric nitrate, rust-colored.

Mercurous salt, rusty precipitate mixed with the black product from the excess of ammonic hydrate.

Cadmium salt, yellowish red.

Lead salt, brilliant rust-color.

Silver salt, vivid brown ("Bismarck brown").

The most characteristic point in its behavior with reagents is that the magnesium and calcium salts are less soluble than the strontium and barium salts, the order of solubility being magnesium and calcium least soluble, strontium more soluble, barium the most soluble. A similar observation has been made by Bischoff[1] in regard to the salts of orthonitrobenzoylmalonic ester, and the bromdinitrophenylacetacetic ester also exhibits the same peculiarity, as we mention in detail in the next paper of this series.

Salts of Bromtrinitrophenylmalonic Ester.

We had intended at first to make a rather thorough study of the salts of the bromtrinitrophenylmalonic ester, but after a few

[1] Ann. Chem. (Liebig) **251**, 362.

experiments became convinced that this would be a waste of time, as, owing to the ease with which the atom of bromine can be removed, no very satisfactory analytical results could be obtained; and we were the more ready to give up this part of the work, because our investigation of the secondary oily product of the reaction, by which the bromtrinitrophenylmalonic ester is formed, had settled beyond a doubt the composition of the ester, which before this and the similar investigation made by one of us and W. S. Robinson had rested principally on the analyses of its salts (see this Journal **II**, 97, 1889). We have confined ourselves therefore to a single analysis of the sodium salt, and a preliminary study of the copper salt, the results of which are given below.

Sodium Salt, $C_6HBr(NO_2)_3CNa(COOC_2H_5)_2$.—This substance was made in two ways. First, by digesting solid pure sodic carbonate with a solution of bromtrinitrophenylmalonic ester in absolute alcohol. The red solution was filtered from the excess of sodic carbonate, evaporated to dryness on the water-bath, and dried at 100°, when it gave the following result on analysis:

0.2373 gram of the salt gave after being heated with sulphuric acid 0.0418 gram of sodic sulphate.

	Calculated for $C_6HBr(NO_2)_3CNa(CO_2C_2H_5)_2$.	Found.
Sodium	4.87	5.71

The bad result is probably due to a slight excess of sodic carbonate, which dissolved in the alcohol. The salt looked black and somewhat decomposed.

The second and better method was that used for making the salt of the corresponding dinitro compound, that is, by the action of an alcoholic solution of sodic hydrate or ethylate on an alcoholic solution of the ester, taking care that the ester is in excess. For the necessary precautions see this Journal **II**, 100, 1889. No analysis was made of this preparation, as from our experience with the acetacetic compound we were sure that no accurate analytical results would be obtained.

Properties.—The sodium salt forms an amorphous blackish red mass, soluble in ethyl or methyl alcohol, water, or acetone; tolerably soluble in ether; slightly in chloroform; insoluble in benzol or ligroin. All the solutions have a deep blood-red color. When the salt is treated with an excess of strong nitric acid (of specific gravity 1.36), it is at first decolorised, but almost immedi-

ately turns vivid red, owing to the formation of the substance produced by warming the free ester with nitric acid. This behavior is characteristic, as it appears with none of the similar substances which we have studied.

Copper Salt.—We took up the study of this salt in the hope of throwing light on the composition of the ester, but after analysing several samples were convinced that the precipitate had a varying composition, and therefore describe our work only because of a curious observation made in the course of it. The salt was made by adding a solution of cupric sulphate to an alcoholic solution of the sodium salt, which need not be free from sodic hydrate; the copper salt was extracted with ether, and obtained on evaporating the ethereal solution as an orange mass, which when heated exploded with a blue flame. It was insoluble in water, nearly insoluble in cold alcohol, soluble in hot, and the yellow solution deposited the salt in rhombic crystals; very soluble in benzol or chloroform, insoluble in ligroin.

We next substituted an alcoholic solution of cupric chloride for the cupric sulphate, in hopes of getting a better result, when to our surprise a product was obtained crystallising from alcohol in long white prisms, and melting in the crude state at 75°. This product was obtained more than once, but as frequent crystallisation was necessary to purify it, we did not at first have enough to bring it into a state fit for analysis; and, on returning to the subject after some months, we obtained under the same conditions nothing but the orange explosive copper salt. Unfortunately, we had postponed work on this subject till so near the end of the term that we were unable to give it the careful study it seems to deserve, but its investigation will be continued in this laboratory next year.

Study of the Reactions by which Bromtrinitrophenylmalonic Ester is formed.

The reactions by which the bromtrinitrophenylmalonic ester is formed from the tribromtrinitrobenzol must consist in the replacement of one of the atoms of bromine by the malonic ester radical $CH(COOC_2H_5)_2$, and of another by hydrogen. The first of these processes needs no explanation, but the mechanism of the second, the replacement of the bromine by hydrogen, could be made out only by experiment. Obviously, the first point to be settled was

the form in which the bromine was eliminated; that is, whether as sodic bromide alone, or partly as sodic bromide and partly as an organic compound. For this purpose the following quantitative determinations were made:

I. 10 grams of tribromtrinitrobenzol, treated with the sodium malonic ester from 15 grams of malonic ester, gave after standing two days and a half 8.83 grams of argentic bromide, corresponding to 3.76 grams of bromine.

II. The same weights under the same conditions gave 9.08 grams of argentic bromide, corresponding to 3.86 grams of bromine.

If two atoms of bromine had been removed, the amount of bromine should have been 3.55 grams. Therefore the percentages of the theoretical bromine removed as sodic bromide were,

I.	II.
105.9	108.8

It appears, therefore, that a little more than the amount calculated for two atoms of bromine has been removed as sodic bromide, and this is easily explained by the observation described later in this paper, that sodium malonic ester can act on the bromtrinitrophenylmalonic ester even in the cold to form the trinitrophenylenedimalonic ester, a small quantity of which was undoubtedly formed in these two experiments by the large excess of sodium malonic ester present. At any rate, there can be no question that all the bromine was removed in the form of sodic bromide.

The next step consisted in determining the nature of the organic secondary product. For this purpose, the oil, separated from the bromtrinitrophenylmalonic ester by sucking out the crude product on the pump and treatment with alcohol, was allowed to stand till it ceased to deposit crystals of the ester, and then submitted to distillation under diminished pressure. The pressure varied from 22 to 25 mm., and a distillate began to appear when the thermometer inside the flask stood at 98°, and was collected until the temperature had reached 160°, when about one-third of the total volume had passed over. In this way a clear yellow liquid was obtained, which distilled unaltered at ordinary pressure between 197° and 206°. We therefore inferred it was mostly malonic ester, boiling point 197.7°, a view of its nature which was confirmed by its smell. As the whole of the distillate passed over below 206°, there could be no large amount of tartronic ester (boiling point 220°) present, which we had expected after the work of one of us and

W. S. Robinson on the corresponding dinitro compound, and the secondary product of the reaction must be looked for in the residue which had been left behind in the flask after the distillation under diminished pressure. This was a thick blackish brown oil, which on standing for about a week deposited crystals all over its surface; these were removed and allowed to stand on filter paper until a large part of the oil had been sucked out, when they were purified by washing with a small quantity of cold alcohol, and then crystallising from boiling alcohol, until they showed the constant melting point 76°. The substance formed long glittering colorless needles or prisms, and contained no bromine: we decided accordingly that it was the acetylentetracarbonic ester (melting point 76°), and this conclusion was confirmed by the following analysis:

0.2270 gram of the substance gave on combustion 0.4384 gram of carbonic dioxide and 0.1506 gram of water.

	Calculated for $C_2H_2(CO_2C_2H_5)_4$.	Found.
Carbon	52.83	52.67
Hydrogen	6.92	7.36

The amount of acetylentetracarbonic ester was so considerable that there can be no doubt it was a principal product of the reactions by which the bromtrinitrophenylmalonic ester is formed, and these must therefore be written thus:

$$C_6Br_3(NO_2)_3 + 3CHNa(COOC_2H_5)_2 =$$
$$C_6Br_2(NO_2)_3CH(COOC_2H_5)_2 + NaBr + 2CHNa(COOC_2H_5)_2 =$$
$$C_6Br_3(NO_2)_3CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2$$
$$+ CHNa(COOC_2H_5)_2 + NaBr =$$
$$C_6HBr(NO_2)_3CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2$$
$$+ CHNa(COOC_2H_5)_2 + NaBr =$$
$$C_6HBr(NO_2)_3CNa(COOC_2H_5)_2 + C_2H_2(COOC_2H_5)_4 + 2NaBr.$$

The only objection which could be urged against this series of reactions is that the yield of bromtrinitrophenylmalonic ester is only 64 per cent. of the theoretical, from which it might be argued that nearly half of the tribromtrinitrobenzol may have undergone some different transformation. This objection is disposed of, however, by the fact that W. D. Bancroft and one of us have succeeded in getting a yield of 80 per cent. of the dibromdinitrophenylmalonic ester from tetrabromdinitrobenzol by a series of reactions exactly analogous to those just given. The missing 36 per cent. of the

bromtrinitrophenylmalonic ester must therefore have remained dissolved in the oil, and have been destroyed by the distillation even under the diminished pressure used by us.

Action of Nitric Acid.

The intense red color produced by the action of nitric acid of specific gravity 1.36 on the sodium, or copper salt of the bromtrinitrophenylmalonic ester in the cold, or on the ester itself at 100°, seemed to us of great interest, and we laid out what we thought would be time enough for its investigation; unfortunately, however, this was not the case, since, after the work had been going on for some time, we found that at least two substances were formed by this reaction, and consequently the end of the term surprised us before we had reached any definite results. We have decided, however, to publish here what results we have obtained, as we are unable to go on with this work together, but wish it to be understood that all these statements are to be taken as preliminary.

If about 1 gram of bromtrinitrophenylmalonic ester was mixed with 2–3 cc. of strong nitric acid (specific gravity 1.36), no change took place in the cold; but if the mixture was warmed gently on the water-bath for less than five minutes, an intense vivid red color appeared in both the acid liquid and the organic substance, which melted and became converted into a viscous mass. If now the acid was poured off, a fresh quantity added, and the gentle warming repeated, the viscous drop became converted into a red crystalline mass, and by continuing this treatment with successive portions of nitric acid the red color could be removed partially, so that the product had a spotted red and white appearance. This frequent treatment with nitric acid was, however, unnecessary, as the red crystalline product after the second warming with nitric acid gave, when crystallised from alcohol, well formed white prisms and a reddish mother liquor. The red nitric acid poured off from the principal part of the product gave with water a red precipitate, but a better mode of treatment seemed to be to evaporate this red acid to dryness on the water-bath. The residue, or precipitate obtained with water, was partly viscous, partly crystalline, and by treating it again with warm strong nitric acid a new quantity of the red crystalline substance was obtained, but the amount recovered in this way was so small that it hardly paid for

the trouble. The white crystals, after purification by crystallisation from alcohol, showed the constant melting point 125°, and their behavior in melting was very characteristic, as they turned from white to bright red, and swelled to many times their original volume. They were not affected by sodic hydrate in aqueous solution. Supposing that the substance was homogeneous because of its constant melting point, we analysed it, but on studying its properties more carefully we began to doubt its purity, for the following reasons: First. Although the microscopic examination showed that the substance consisted principally of white, short, rather thick monoclinic prisms, usually with both terminations well developed and made up of two planes, there were mixed with these longer prisms, and we could not decide whether these latter were a different substance or merely a different habit of the same. Second. When the crystals were treated with sodic hydrate and alcohol a little of a soluble red salt was formed around each crystal, but we could not convert the whole of the crystals into this salt. This seemed to point to the presence of an impurity, from which the salt was formed. Third. We found, almost at the very end of the term, that by warming the bromtrinitrophenylmalonic ester with strong nitric acid for three hours, instead of a few minutes, a red substance was obtained which crystallised from alcohol, became white, and melted at 156° instead of 125°, and, what was as distinctive as the different melting point, fused to a colorless liquid, and gave a red solution with aqueous sodic hydrate. This substance was discovered so late that we had no time to investigate it, but some of it seemed to be formed even on shorter heating (15 minutes) with the nitric acid. For these reasons we have decided that it is wiser to postpone the publication of our analyses of the substance melting at 125° until the work has been repeated with samples in regard to the purity of which there can be no doubt. We add such results of our work as are established with certainty. The analyses made by us showed that there were three atoms of nitrogen to one of bromine in the substance, and therefore the action of the nitric acid did not consist in the introduction of another nitro, or nitroso group. The fact that it is insoluble in aqueous sodic hydrate shows that it is not a free acid, and its action with hydrochloric acid would indicate that it was an ester, as, when heated to 135°–140° with this acid in a sealed tube for 36 hours, a gas was given off burning with a green-bordered flame, and giving a white precipitate

with lime-water, which therefore must have contained ethyl chloride and carbonic dioxide. The solid product of this action was partly viscous and partly crystalline; the latter melted in the crude state above 180°. It has been stated already that the substance melting at 125° turns red and increases in volume when it melts; this change, which takes place to a limited extent even when it is kept at 100° for some time, is accompanied by loss of weight, as a sample kept at its melting point for some days lost at least 17 per cent., and gave a residue consisting of two or more substances, one white and crystalline, the other red and viscous.

Action of Sulphuric Acid.— Constitution of the Bromtrinitrophenylmalonic Ester.

The action of dilute sulphuric acid upon the bromtrinitrophenylmalonic ester was studied in the hope of obtaining the as yet unknown bromtrinitrophenylacetic acid, as it had been found by one of us and W. S. Robinson[1] that the corresponding dinitro compound was decomposed in this way. For this purpose, about 2 grams of the ester were boiled in a flask under a return condenser with sulphuric acid of specific gravity 1.44 and boiling point 132° until the ester had dissolved; the liquid was then allowed to cool, when it deposited crystals, which, after recrystallisation from alcohol, were recognised by their melting point 143°–144°, their appearance, and the absence of acid properties, as the metabromtrinitrotoluol discovered in this laboratory by Bentley and Warren.

It is evident therefore that the bromtrinitrophenylacetic acid is less stable than the corresponding dinitro compound, as indeed was to be expected, and was broken up as soon as formed into the substituted toluol and carbonic dioxide, according to the following reaction:

$$C_6HBr(NO_2)_3CH_2COOH = C_6HBr(NO_2)_3CH_3 + CO_2.$$

The formation of this substance would settle the constitution of the bromtrinitrophenylmalonic ester, if that were necessary, but the preparation of the ester from symmetrical tribromtrinitrobenzol leaves no doubt as to its constitution, which must be as follows, $CH(COOC_2H_5)_2$, NO_2, Br, NO_2, H, NO_2, 1, 2, 3, 4, 5, 6, and Bentley and Warren have established the corresponding constitution for their substituted toluol.

[1] This Journal **11**.

Trinitrophenylendimalonic Ester, $C_6H(NO_2)_3[CH(COOC_2H_5)_2]_2$.

This substance was formed by the further action of sodium malonic ester on bromtrinitrophenylmalonic ester. For this purpose, 1 gram of bromtrinitrophenylmalonic ester dissolved in ether was mixed with 1.5 gram of malonic ester previously converted into sodium malonic ester and dissolved in much absolute alcohol, and the mixture boiled in a flask with a return condenser for an hour. The product, which was very dark brown, almost black, was treated with water, acidified with dilute sulphuric acid avoiding a large excess, the ether removed with a drop funnel, and the aqueous liquid shaken out twice with ether. The extract, after distilling off the ether and allowing it to get perfectly cool, was treated with a little alcohol, when crystals separated on standing, which were purified by recrystallisation from alcohol, until they showed the constant melting point 123°. They gave no test for bromine when heated on a copper wire, and, after drying *in vacuo*, were analysed with the following results:

I. 0.3004 gram of the substance gave on combustion 0.5043 gram of carbonic dioxide and 0.1230 gram of water.

II. 0.2392 gram of the substance gave 16.8 cc. of nitrogen at a temperature of 25° and a pressure of 768 mm.

	Calculated for $C_6H(NO_2)_3[CH(COOC_2H_5)_2]_2$.	Found. I.	II.
Carbon	45.37	45.78	
Hydrogen	4.35	4.55	
Nitrogen	7.94		7.92

A small quantity of this substance can also be formed in the cold, and more than once some of it has been obtained in making the bromtrinitrophenylmalonic ester by the process described earlier in this paper.

Properties.—The trinitrophenylendimalonic ester crystallises from alcohol in long colorless prisms, terminated by a single rhombic plane at a tolerably sharp angle to the sides; less frequently, the termination consists of two planes at an obtuse angle to each other, so that the general effect is as if the prisms had rounded ends. They are frequently grouped, or twinned, parallel to their long axes, so that often there are two or more terminations at one end of a group. The substance melts at 123°, and is very nearly, if not quite, insoluble in water, whether cold or boiling; essentially insoluble in ligroin; not very soluble in cold ethyl or

methyl alcohol, freely in either of these solvents when hot; very slightly soluble in carbonic disulphide; soluble in ether or glacial acetic acid, and freely soluble in benzol, chloroform, or acetone. Its acid properties are not so strongly developed as we expected. An aqueous solution of sodic hydrate turns the solid pale red, but does not dissolve it to any extent; if, however, solid hydrate is added to its alcoholic solution, it at once takes on a dark brownish red color, much browner than any of the similar salts which we have studied—in fact it would be possible to recognise the salt by this color. An aqueous solution of potassic carbonate gives a very faint red color with it, which is increased, but not to a great extent, by adding alcohol to the aqueous solution. The action was incomplete at best; acid sodic carbonate had no action on it in aqueous solution, but on the addition of alcohol a barely perceptible red color appeared. Ammonic hydrate even in dilute aqueous solution dissolved it easily with a brown color; the solution turned blacker when the attempt was made to drive off the excess of ammonia on the water-bath, and a white scum formed on the surface, probably the original substance. The behavior of this solution was studied with some of the commoner reagents; but, as it showed such evident signs of decomposition, we did not think it worth while to extend this work to salts of all the basic radicals.

Ferric salt, *cupric salt*, *silver salt*, and *lead salt* all gave brown flocculent precipitates.

Calcium salt gave no precipitate.

Barium salt, a very slight dirty brown precipitate, but none if the solution had not been warmed on the water-bath in the vain attempt to drive off the excess of ammonia.

Strong sulphuric acid dissolved the dimalonic ester, giving a colorless solution. Strong hydrochloric acid had no action upon it, whether hot or cold. Strong nitric acid dissolved it partially in the cold, giving a yellowish solution, which when warmed became darker yellow; but if the warming on the water-bath was continued for some time, the acid liquid became red, and a red viscous substance was also obtained, which, after washing with water and crystallisation from alcohol, was converted into yellow plates melting at 104°–105° in the crude state. It is evident that the action here is similar to that of bromtrinitrophenylmalonic ester with strong nitric acid, but the end of the term has prevented us from continuing the study of this substance at present.

LXVII.—ON CHLORPYROMUCIC ACIDS.[1]

By Henry B. Hill and Louis L. Jackson.

Many years ago Malaguti[2] found that dry chlorine gas was quickly absorbed by ethyl pyromucate, and that a thick viscous liquid was formed, the composition of which showed that four atoms of chlorine had been taken up. The oil was carbonised on distillation, and yielded with potassic hydrate decomposition products which were not further studied. Although Schmelz and Beilstein[3] later found that chlorine converted pyromucic acid in aqueous solution into mucochloric acid, and this reaction was afterwards further studied by Hill and Bennett,[4] no further experiments, as far as we could learn, had ever been made with dry chlorine on pyromucic acid or its ethers. In 1884, after it had been shown by investigations carried on in this laboratory that substitution products could readily be formed from pyromucic acid by the action of dry bromine, Mr. J. N. Garratt, at that time an assistant in the laboratory, undertook the investigation of the action of dry chlorine under similar conditions. Although he succeeded in isolating a dichlorpyromucic acid melting at 167°–168° in a state of purity, he found that the reaction differed in many respects from the corresponding reaction with bromine, and that the matter deserved a more careful study than he was then able to bestow upon it. Mr. Garratt relinquished his investigation of this subject in order to continue his studies in Zurich, and in the following winter met with the fatal accident which so sadly ended his promising career.

The observations which already had been made interested us so much that in 1886 we undertook a more thorough study of the subject. We had already collected a great deal of material which we did not think it necessary to publish in a preliminary form, when Denaro[5] published in the Gazzetta Chimica a brief notice of a dichlorpyromucic acid melting at 167°–168°, which was evidently identical with that prepared by Garratt. The paper contained a description of the acid and two of its salts, but the

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences. A part of the work described in the following paper was presented in the form of a thesis to the Academic Council of Harvard University, in May, 1888, by Louis L. Jackson, then candidate for the degree of Doctor of Philosophy.

[2] Ann. Chim. Phys. **64**, 282; **70**, 371.

[3] Ann. Chem. (Liebig), Suppl. **3**, 276.

[4] Ber. d. chem. Ges. **12**, 655.

[5] Gazz. chim. ital. **16**, 333.

analyses of the latter did not agree with those which we had already obtained, and moreover contained such serious misprints or arithmetical errors, or both, as to be wholly without value. In consequence of the appearance of that paper, we thought it best to publish a preliminary account[1] of our work, so far as that one acid was concerned, more especially since our study of it was then essentially completed.

In repeating the experiments of Garratt, we had no difficulty in isolating the dichlorpyromucic acid which he had prepared, but we found that the reaction was still more complex than we had supposed. At ordinary temperatures chlorine was rapidly absorbed, but the pyromucic acid was soon so coated with the viscous addition-product that a homogeneous product could not be obtained. On heating, the reaction could easily be pushed to the end, and the gain in weight closely corresponded with the addition of four atoms of chlorine. At the same time hydrochloric acid and carbonic dioxide were given off, and the resulting product contained a percentage of chlorine much larger than that demanded by any simple addition-product. Under these circumstances it seemed advisable to return to the ethyl pyromucic tetrachloride of Malaguti, which, from his description and analyses, appeared to be homogeneous; and to take up the study of the more complex action of chlorine upon the acid itself after this investigation had made us better acquainted with some of the products likely to be formed. Although we were unable to prepare a perfectly homogeneous product by following the directions of Malaguti, we found no difficulty in so modifying the conditions that the resulting compound should give us pure $\beta\gamma$-dichlorpyromucic acid melting at 168°–169°, δ-chlorpyromucic acid melting at 176°–177°, or trichlorpyromucic acid melting at 172°–173°. The $\beta\delta$-dichlorpyromucic acid we were unable to prepare by direct substitution, or by saponification of ethyl pyromucic tetrachloride; but by distillation of ethyl pyromucic tetrachloride, of the tetrachloride of pyromucyl chloride, or of ethyl δ-chlorpyromucic tetrachloride, the $\beta\delta$-dichlorpyromucic acid melting at 155°–156° may be obtained, and in the first two cases a third dichlorpyromucic acid melting at 197°–198° is also formed. By careful reduction of the $\beta\delta$- or the $\beta\gamma$-dichlorpyromucic acids, the β-chlorpyromucic acid melting at 145°–146° is formed.

[1] Ber. d. chem. Ges. **20**, 252.

Ethyl Pyromucic Tetrachloride.

The ethyl pyromucate which we have used in the course of our investigations we have made by warming a solution of pyromucic acid (3 parts) in absolute alcohol (5 parts) with concentrated sulphuric acid (3 parts acid, sp. gr. 1.84). After heating for four hours on the water-bath, the mixture was allowed to cool, precipitated with water, and the ether washed with a dilute solution of sodic carbonate. The crude ether was then dried by exposure to the air and distilled. The yield of pure distilled ether which is thus obtained amounts to about 85 per cent. of the weight of the acid taken. This is somewhat less than that which may be obtained by means of hydrochloric acid, but the method is much more expeditious and convenient.

When dry chlorine is passed over ethyl pyromucate we found that the ether was rapidly liquefied with the evolution of heat, and that the formation of the addition-product proceeds as described by Malaguti until the ether has increased in weight very nearly the amount required by the addition of four atoms of chlorine. We soon found, however, that, no matter how carefully the chlorine was dried, hydrochloric acid escaped, showing the formation of a substitution product, and that the amount of hydrochloric acid formed depended largely upon the rapidity of the stream of chlorine and the consequent elevation of temperature. Even when the ether was carefully cooled to 0° during the whole of the treatment with chlorine, the formation of hydrochloric acid could not wholly be avoided. In this respect our experience agrees with that of Hill and Sanger,[1] who were unable to form the ethyl pyromucic tetrabromide without the simultaneous formation of substitution products. While the statements of Malaguti seemed to leave no room for doubt that the ethyl pyromucic tetrachloride was completely carbonised by heat, experiments made with bromine in this laboratory had shown that substitution products could readily be formed from the ethyl pyromucic tetrabromide by heat, and it seemed to us hardly conceivable that complete carbonisation should ensue. A preliminary trial showed so much less charring under ordinary pressure than we had anticipated, that we were encouraged to hope that the ethyl pyromucic tetrachloride itself might be distilled under diminished pressure without essential decomposition. Ethyl pyromucate was there-

[1] Proc. Am. Acad. 21, 155.

fore carefully treated with chlorine at 0° until it ceased to gain in weight. Hydrochloric acid was given off in small quantity, and the total gain in weight was 94 per cent. of the weight of ethyl pyromucate taken, instead of the theoretical gain of 101 per cent. The product was then fractionally distilled under a pressure of 15 mm., and showed its complex nature by the wide range of its boiling point, 104°–160°. Above 160° there remained a residue which, even under 15 mm. pressure, could not be distilled without decomposition.

None of the fractions showed any tendency to solidify in a freezing mixture. After several distillations, it became evident that the greater portion boiled without essential decomposition between 150°–160°, and that smaller portion boiled below 110°.

In order to determine the nature of the several products, the following analyses were made. Each fraction was collected under 15 mm. pressure.

A. Boiling point 104°–110°; weight = 2.6 grams.
0.2235 gram substance gave 0.2139 gram AgCl.

	Calculated for $C_8H_9ClO_3C_2H_5$.	Found.
Cl	20.34	23.63

B. Boiling point 145°–150°; weight = 3.2 grams.
0.2334 gram substance gave 0.4418 gram AgCl.

C. Boiling point 152°–153°; weight = 7.7 grams.
I. 0.1678 gram substance gave 0.3431 gram AgCl.
II. 0.1415 gram substance gave 0.2889 gram AgCl.

D. Boiling point 153°–157°; weight = 12.0 grams.
0.1502 gram substance gave 0.3094 gram AgCl.

	Calculated for $C_8H_9O_3C_2H_5Cl_4$.	B.	Found. C. I.	C. II.	D.
Cl	50.36	46.77	50.55	50.49	50.97

From these analyses it was evident that the fraction C consisted of pure ethyl pyromucic tetrachloride; the fraction D contained a slight admixture of a product containing a higher percentage of chlorine; the fraction A approached in composition the ethyl chlorpyromucate; while the fraction B was a mixture. In order to be quite sure of the correctness of our conclusions, we treated these successive fractions with an alcoholic solution of sodic hydrate, and obtained acids in each case confirming the results of

our analyses. From fraction A we obtained an acid crystallising from hot water in irregular leafy plates which melted at 176°–177°. The physical properties and melting point were sufficient to identify this acid as the δ-chlorpyromucic acid later described, and to prove that the lower boiling fraction consisted chiefly of ethyl δ-chlorpyromucate. Fraction C yielded us without difficulty, and in nearly theoretical quantity, an acid which, when recrystallised twice from benzol, melted sharply at 168°–169°, and in other respects proved to be identical with the $\beta\gamma$-dichlorpyromucic acid which we shall hereafter fully describe. The formation of this acid in nearly theoretical quantity and without recognisable admixture proves that the fraction C consisted of pure ethyl pyromucic tetrachloride. Fraction D yielded us a somewhat less pure $\beta\gamma$-dichlorpyromucic acid, as did also fraction B. In the latter case, however, we were able to isolate a small quantity of a sparingly soluble acid, crystallising from water in minute needles which closely resembled trichlorpyromucic acid. It was therefore evident that the main product formed by the action of chlorine at o° upon ethyl pyromucate was the tetrachloride, and this might be distilled under diminished pressure without essential decomposition. At the same time it was shown that substitution was effected even in the cold, and that the product contained ethyl δ-chlorpyromucate and very possibly its tetrachloride.

δ-Chlorpyromucic Acid.

Since substitution had taken place at low temperatures, it seemed not unlikely that at 100° the substitution might be so rapid as to offer a convenient mode for the preparation of chlorpyromucic acids. Ethyl pyromucate, when treated with bromine at 100°, yields δ-brompyromucic and $\beta\delta$-brompyromucic acids still more readily than pyromucic acid itself. We accordingly passed dry chlorine through ethyl pyromucate heated to 100°, but found that a higher temperature was necessary in order that the substitution might promptly be effected. At 145° the action was sufficiently rapid, and the chlorine was passed through the melted ether at this temperature until a gain in weight was noted which corresponded to the substitution of one hydrogen atom by chlorine. The viscous liquid which was thus obtained was then slowly added to an excess of a concentrated alcoholic solution of sodic hydrate, care being taken to avoid any great elevation of temper-

ature. When the action was completed the sparingly soluble sodium salt was removed by filtration and dried. The alcoholic filtrate contained small quantities of this sodium salt in solution, and contained further a small amount of some volatile furfuran compound. We converted the excess of sodic hydrate into carbonate with carbonic dioxide, removed the sodic carbonate by filtration, and distilled the alcoholic filtrate. The distillate when mixed with water threw down a minute quantity of a colorless oil of peculiar aromatic odor, which we have as yet been unable to identify through lack of material. The small amount of sodium salt obtained from the alcoholic mother liquors was then added to the main portion. The sodium salt when dissolved in water and acidified with hydrochloric acid then yielded the crude δ-chlorpyromucic acid, which not infrequently needed no other purification than recrystallisation from benzol. If, however, the treatment with chlorine had been too long continued, or the action had taken place at too low a temperature, the product contained dichlorpyromucic and trichlorpyromucic acids which could not be removed by simple recrystallisation. Whenever the crude acid failed on trial to crystallise from hot water in shining irregular plates, it was necessary to resort to chemical means for its purification. The acid was suspended in twenty times its weight of cold water, ammonia added in slight excess, and then baric chloride in quantity sufficient to precipitate the sparingly soluble barium salts of the admixed acids. After the separation of these salts is complete, the filtered solution gives on acidification an acid which crystallises from water in leafy plates, and which may further be purified by recrystallisation from benzol. The yield of chlorpyromucic acid thus obtained amounts to about 40 per cent. of the weight of ether taken, or 38 per cent. of the theoretical amount.

I. 0.2761 gram substance gave 0.4145 gram CO_2 and 0.0494 gram H_2O.

II. 0.2667 gram substance gave 0.2642 gram AgCl.

III. 0.2990 gram substance gave 0.2950 gram AgCl.

	Calculated for $C_5H_3ClO_3$.	Found. I.	II.	III.
C	40.96	40.94	...	...
H	2.05	1.99	...	...
Cl	24.23	...	24.49	24.39

The δ-chlorpyromucic acid is readily soluble in hot water, sparingly in cold water, and crystallises in large irregular leafy plates, which closely resemble the corresponding bromine derivative. It dissolves readily in alcohol, ether, or hot benzol, but sparingly in cold benzol. The acid recrystallised from benzol melted at 176°–177°, and a preparation made from the pure ethyl ether melted at the same point. Its solubility in cold water was determined according to the method of V. Meyer. A weighed portion of the solution saturated at 19.5° was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid.

I. 37.8458 grams solution saturated at 19.5° gave 0.0833 gram $BaSO_4$.

II. 33.5216 grams solution saturated at 19.5° gave 0.0742 gram $BaSO_4$.

According to these determinations, the solution saturated at 19.5° contained the following percentages of acid:

I.	II.
0.28	0.28

Baric δ-chlorpyromucate, $Ba(C_5H_2ClO_3)_2.H_2O$.—The barium salt was prepared by boiling the acid with an excess of baric carbonate. The salt is quite readily soluble even in cold water, still more readily soluble in hot water, and separates from a hot concentrated solution in thin leafy plates, usually aggregated in globular form. The air-dried salt contains one molecule of water, which it loses rapidly at 100°.

I. 1.2193 gram air-dried salt lost at 100° 0.0491 gram H_2O.

II. 0.5932 gram air-dried salt gave 0.3094 gram $BaSO_4$.

	Calculated for $Ba(C_5H_2ClO_3)_2.H_2O$.	Found. I.	II.
H_2O	4.04	4.04	...
Ba	30.72	...	30.67

0.6909 gram salt dried at 100° gave 0.3763 gram $BaSO_4$.

	Calculated for $Ba(C_5H_2ClO_3)_2$	Found.
Ba	32.01	32.02

The solubility of the salt in cold water was determined according to the method of V. Meyer.

I. 9.3523 grams solution saturated at 19.5° gave 0.2932 gram $BaSO_4$.

II. 8.3395 grams solution saturated at 19.5° gave 0.2534 gram $BaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
5.76	5.58

Calcic δ-chlorpyromucate, $Ca(C_5H_2ClO_3)_2.3H_2O$.—The calcium salt was prepared by boiling the acid with an excess of calcic carbonate. It is readily soluble in hot water, rather sparingly soluble in cold water, and separates from a hot concentrated solution in clustered prisms with rectangular terminations. The air-dried salt contains three molecules of water. It effloresces slowly over sulphuric acid, and loses all its water readily at 100°.

I. 1.0814 gram air-dried salt lost at 100° 0.1480 gram H_2O.

II. 1.2247 gram air-dried salt lost at 100° 0.1689 gram H_2O.

	Calculated for $Ca(C_5H_2ClO_3)_2.3H_2O$.	Found. I.	II.
H_2O	14.03	13.70	13.79

I. 0.6236 gram salt dried at 100° gave 0.2564 gram $CaSO_4$.

II. 0.5509 gram salt dried at 100° gave 0.2244 gram $CaSO_4$.

	Calculated for $Ca(C_5H_2ClO_3)_2$.	Found. I.	II.
Ca	12.09	12.09	11.98

The solubility of the salt in cold water was determined according to the method of V. Meyer. The calcium was precipitated as oxalate, and the oxalate ignited with sulphuric acid.

I. 21.6494 grams solution saturated at 19.5° gave 0.1002 gram $CaSO_4$.

II. 17.7467 grams solution saturated at 19.5° gave 0.0809 gram $CaSO_4$.

The solution saturated at 19.5° contained therefore the following percentages of anhydrous salt:

I.	II.
1.13	1.11

Potassic δ-chlorpyromucate, $KC_5H_2ClO_3$.—The potassium salt is readily soluble even in cold water, and separates from a hot concentrated solution on rapid cooling in fine branching needles; on slower cooling, in small thin oblique plates. The salt lost nothing in weight when dried at 120°, and analysis showed it to be anhydrous.

I. 0.6543 gram salt dried at 120° gave 0.3100 gram K_2SO_4.
II. 0.6390 gram salt dried at 120° gave 0.3018 gram K_2SO_4.

	Calculated for $KC_5H_2ClO_3$.	Found. I.	II.
K	21.18	21.27	21.20

Argentic δ-chlorpyromucate, $AgC_5H_2ClO_3$.—The silver salt may best be prepared by precipitating a solution of the barium salt with argentic nitrate.

For analysis the precipitated salt was well washed, recrystallised from hot water, and dried *in vacuo* over sulphuric acid. It is sparingly soluble even in hot water, and separates from a hot concentrated solution in irregularly branching flattened needles.

I. 0.4843 gram substance gave 0.2730 gram AgCl.
II. 0.3948 gram substance gave 0.2220 gram AgCl.

	Calculated for $AgC_5H_2ClO_3$.	Found. I.	II.
Ag	42.60	42.44	42.34

Ethyl δ-chlorpyromucate, $C_5H_2ClO_3C_2H_5$.—The ethyl ether was prepared by heating at 100° a solution of 5 parts of δ-chlorpyromucic acid in 10 parts of absolute alcohol, with the addition of 5 parts of concentrated sulphuric acid (sp. gr. 1.84).

After heating for three hours, the ether was precipitated by the addition of water, washed first with dilute sodic carbonate, then with water, and finally dried with calcic chloride. The ether is a colorless heavy oil boiling at 216°–218° (column completely in vapor) under a pressure of 76.8 mm., solidifying at 1°–2°, and melting at the same point.

I. 0.2740 gram substance gave 0.2219 gram AgCl.
II. 0.2918 gram substance gave 0.2402 gram AgCl.

	Calculated for $C_5H_2ClO_3C_2H_5$.	Found. I.	II.
Cl	20.34	20.02	20.35

δ-Chlorpyromucamide, $C_5H_2ClO_2NH_2$.—δ-Chlorpyromucic ether is but slowly attacked by concentrated ammonia in the cold, and the amide may more readily be prepared from the acid chloride by means of solid ammonic carbonate. The amide is readily soluble in hot water, sparingly soluble in cold water, and separates from a hot concentrated solution in fine branching needles, which melt at 154°–155°.

For analysis, the amide was dried over sulphuric acid.

I. 0.1696 gram substance gave 0.1677 gram AgCl.

II. 0.2933 gram substance gave 25.7 cc. moist N at 25° and under a pressure of 764 mm.

	Calculated for $C_5H_2ClO_3NH_2$.	Found. I.	II.
Cl	24.40	24.44	...
N	9.62	...	9.82

Preparation I was made from the ether, and II from the acid chloride.

There seemed no room for doubt that the chlorpyromucic acid thus formed by the direct replacement of hydrogen by chlorine, like the δ-brompyromucic acid obtained in a similar way, contained its chlorine in the δ position. We considered it necessary, however, to establish this point by direct experiment.

Action of Bromine and Water.

Although the action of bromine on δ-brompyromucic acid suspended in water varied greatly with the conditions, Hill and Sanger[1] found that, when the oxidation was carefully conducted, fumaric acid alone was formed. We therefore suspended the δ-chlorpyromucic acid in about twenty-five times its weight of water, and passed in bromine vapor slowly with a current of air. The acid gradually dissolved, and but little more than two molecules of bromine were needed to complete the oxidation. After standing for some time in the cold, the solution was evaporated to a small volume, and the crystalline acid which appeared as the solution cooled recrystallised from hot water. In this way we obtained a white crystalline acid which contained neither chlorine nor bromine, which was sparingly soluble in cold water, more readily in hot water, and which remained unchanged when heated to 200°. Although the acid was thus sufficiently characterised as fumaric acid we further analysed its silver salt.

0.4943 gram substance dried at 120° gave 0.5591 gram AgBr.

	Calculated for $Ag_2C_4H_2O_4$.	Found.
Ag	65.46	64.97

In the oxidation of the δ-chlorpyromucic acid by bromine water, fumaric acid had therefore been formed according to the equation:

$$C_5H_3ClO_3 + 2Br_2 + 3H_2O = C_4H_4O_4 + CO_2 + 2HBr + HCl.$$

[1] Proc. Am. Acad. **21**, 144.

Action of Nitric Acid.

δ-Chlorpyromucic acid is not as readily attacked by nitric acid as the δ-brompyromucic acid, and for its complete oxidation we found it necessary to heat one part of the acid with three parts of strong nitric acid (sp. gr. 1.42) diluted with twice its weight of water. After heating for three hours the oxidation was completed, and on evaporation fumaric acid was obtained, which was recognised by its sufficiently characteristic physical properties.

β-Chlorpyromucic Acid.

Hill and Sanger[1] found no difficulty in preparing β-brompyromucic acid by the reduction of either of the two dibrompyromucic acids described by them. The corresponding dichlorpyromucic acids we found to be much more refractory, and we succeeded in preparing the β-chlorpyromucic acid only after many unsuccessful attempts. The $\beta\gamma$-dichlorpyromucic acid, which was the more accessible, proved to be the more difficult of reduction, so that almost the whole of the material for this investigation was made from the $\beta\delta$-dichlorpyromucic acid. When zinc dust is added to a cold ammoniacal solution of this acid, no perceptible reaction takes place, and even after long standing no essential change can be detected. Even when the ammoniacal solution is boiled with a large excess of zinc dust the reduction is but slowly effected, and long continued heating is necessary to complete the reaction. We have found it advantageous to dissolve the acid in about twenty times its weight of dilute ammonic hydrate, to add an equal weight of zinc dust, and to boil for eight or ten hours, taking care to keep the solution strongly ammoniacal. The filtered solution is then cooled and acidified with dilute sulphuric acid, the acid which separates removed by filtration, the filtrate extracted with ether, and the residue left upon the evaporation of the ether added to the main product. The crude acid thus obtained melted at about 130°, and evidently contained unaltered $\beta\delta$-dichlorpyromucic acid. We therefore dissolved it in dilute ammonic hydrate, and added to the ammoniacal solution calcic chloride as long as a sparingly soluble calcium salt was promptly precipitated. The filtered solution then gave, when acidified with hydrochloric acid, a crystalline acid, which after recrystallisation from hot water

[1] Proc. Am. Acad. 21, 147.

melted at 145°–146°, and proved upon analysis to be a chlorpyromucic acid. From the sparingly soluble calcium salt, which had been removed by filtration, we obtained only unaltered $\beta\delta$-dichlorpyromucic acid, which in its turn was treated with zinc dust. In this way we found it possible to obtain from the $\beta\delta$-dichlorpyromucic acid at least 80 per cent. of the theoretical amount of pure β-chlorpyromucic acid. Zinc dust, even after long boiling, seems to have but little action upon $\beta\gamma$-dichlorpyromucic acid in ammoniacal solution, but sodium amalgam slowly reduces it at 100°. In order to effect complete reduction, it proved to be necessary to use a large excess of sodium in the form of a one per cent. amalgam, and the reaction was then completed after heating for three hours on the water-bath. The acid obtained by acidification melted at 145°–146°, contained the percentage of chlorine required by a chlorpyromucic acid, and appeared to be in all respects identical with the acid obtained from the $\beta\delta$-dichlorpyromucic acid. While the yield of pure acid was in this case but 50 per cent. of the theoretical amount, it is possible that it might be somewhat increased by further experiments. From the third isomeric dichlorpyromucic acid, subsequently described, we have as yet been able to obtain no definite reduction product.

The β-chlorpyromucic acid dried over sulphuric acid gave on analysis the following results:

I. 0.2710 gram substance gave 0.4073 gram CO_2 and 0.0513 gram H_2O.

II. 0.1385 gram substance gave 0.1355 gram AgCl.

III. 0.1736 gram substance gave 0.1692 gram AgCl.

	Calculated for $C_4H_3ClO_3$.	Found. I.	II.	III.
C	40.96	40.99	...	...
H	2.05	2.10	...	...
Cl	24.23	...	24.18	24.10

Analysis III was made with material prepared from the $\beta\gamma$-dichlorpyromucic acid.

β-Chlorpyromucic acid is readily soluble in hot water, sparingly soluble in cold water, and crystallises from hot aqueous solution in thin irregular striated plates or flattened prisms. It is readily soluble in alcohol, ether, hot benzol or hot chloroform, and is but sparingly soluble in cold benzol or cold chloroform. When repeatedly crystallised from hot water it melted at 145°–146°, and

recrystallisation from other solvents failed to raise this melting point.

In order to determine the solubility of the acid in cold water, a weighed quantity of a solution of the acid saturated at 19.8° was boiled with baric carbonate, and the barium taken into solution precipitated as sulphate.

I. 31.6300 grams solution saturated at 19.8° gave 0.2019 gram $BaSO_4$.

II. 34.0328 grams solution saturated at 19.8° gave 0.2176 gram $BaSO_4$.

The solution saturated at 19.8° therefore contained the following percentages of the acid:

I.	II.
0.80	0.80

For the further characterisation of the acid we prepared certain of its salts.

Baric β-chlorpyromucate, $Ba(C_5H_2ClO_3)_2.H_2O$.—The barium salt was prepared by boiling a solution of the acid with an excess of baric carbonate. The filtered solution was evaporated, and the salt which separated on cooling recrystallised from hot water. It proved to be readily soluble in hot water, more sparingly soluble in cold water, and crystallised in long obliquely terminated prisms which contained one molecule of water. The salt is permanent in the air or over sulphuric acid, but loses its water readily at 100°.

I. 0.6092 gram of the air-dried salt gave 0.3180 gram $BaSO_4$.

II. 1.3540 gram of the air-dried salt lost at 100° 0.0576 gram H_2O.

	Calculated for $Ba(C_5H_2ClO_3)_2.H_2O$.	Found. I.	Found. II.
Ba	30.72	30.69	...
H_2O	4.04	...	4.25

0.4749 gram of the salt dried at 100° gave 0.2587 gram $BaSO_4$.

	Calculated for $Ba(C_5H_2ClO_3)_2$.	Found.
Ba	32.01	32.03

The solubility of the salt in cold water was determined in the usual way.

I. 10.2683 grams solution saturated at 19.1° gave 0.1149 gram $BaSO_4$.

II. 6.8737 grams solution saturated at 19.1° gave 0.0747 gram $BaSO_4$.

According to these determinations, the aqueous solution saturated at 19.1° contained the following percentages of the anhydrous salt:

I.	II.
2.06	2.00

Calcic β-chlorpyromucate, $Ca(C_5H_2ClO_3)_2.3H_2O$.—This salt was prepared by neutralising with calcic carbonate a boiling solution of the acid. If the solution thus obtained is evaporated upon the water-bath, clustered, pointed prisms of an anhydrous salt are formed when the solution becomes highly concentrated. By evaporation *in vacuo* over sulphuric acid at ordinary temperatures, tufts of fine branching prisms are obtained which contain three molecules of water. The latter salt is permanent in the air, effloresces over sulphuric acid, and loses its water readily at 105°.

I. 0.4226 gram of the air-dried salt gave 0.1490 gram $CaSO_4$.

II. 1.3627 gram of the air-dried salt lost at 105° 0.1902 gram H_2O.

	Calculated for $Ca(C_5H_2ClO_3)_2.3H_2O$.	Found. I.	Found. II.
Ca	10.39	10.37	...
H_2O	14.03	...	13.95

0.5160 gram of the salt dried at 105° gave 0.2111 gram $CaSO_4$.

	Calculated for $Ca(C_5H_2ClO_3)_2$.	Found.
Ca	12.09	12.03

The pointed prisms obtained by evaporating the solution at 100° gave the following results:

0.4433 gram of the air-dried salt gave 0.1796 gram $CaSO_4$.

	Calculated for $Ca(C_5H_2ClO_3)_2$.	Found.
Ca	12.09	11.92

The solubility of the calcium salt in cold water was determined in the usual manner. The calcium was precipitated as oxalate, and converted into the sulphate before weighing.

I. 5.0960 grams solution saturated at 19.5° gave 0.0653 gram $CaSO_4$.

II. 5.8981 grams solution saturated at 19.5° gave 0.0752 gram $CaSO_4$.

According to these determinations, the aqueous solution saturated at 19.5° contained the following percentages of the anhydrous salt:

I.	II.
3.12	3.10

Ethyl β-chlorpyromucate, $C_5H_2ClO_2.C_2H_5$.—The ethyl ether was prepared by heating at 100° for four hours a mixture of 2 parts of the acid, 3 parts of absolute alcohol, and 2 parts of sulphuric acid (sp. gr. 1.84). On dilution with water, the ether separated as an oil, which was thoroughly washed and dried over calcic chloride. It then distilled without essential decomposition at 217° (mercury column completely in vapor) under a pressure of 764 mm. The liquid distillate solidified on cooling, with the formation of concentrically grouped prisms, which, after repeated recrystallisation by cooling the melted ether, showed the constant melting point of 29°–30°.

0.1864 gram of substance gave 0.1523 gram AgCl.

	Calculated for $C_5H_2ClO_2.C_2H_5$.	Found.
Cl	20.34	20.19

Action of Nitric Acid.

β-Chlorpyromucic acid is readily attacked by dilute nitric acid, but the oxidation is not smoothly effected, and the yield of chlorfumaric acid is comparatively small. The best results were obtained when the acid was boiled with 2 parts of nitric acid (sp. gr. 1.42) diluted with 5 parts of water. After the lapse of two hours, the action appeared to be completed, although a few drops of oil were still suspended in the clear solution. The products of the reaction were then extracted from the diluted solution with ether, the residue obtained by the evaporation of the ether pressed thoroughly with filter-paper and dried at 100°. The dry residue was then repeatedly washed with benzol, in which chlorfumaric acid is but sparingly soluble. The product thus obtained was readily soluble in water, almost insoluble in benzol, melted at 188°, and contained the percentage of chlorine required by chlorfumaric acid.[1]

0.1089 gram substance dried over H_2SO_4 gave 0.1027 gram AgCl

[1] Kauder (J. prakt. Chem. [2] **21**, 28) gives the melting point of chlorfumaric acid as 191°.

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.59	23.31

The reaction may therefore be represented, in part at least, by the equation

$$C_5H_3ClO_3 + 3O = C_4H_3ClO_4 + CO_2.$$

Action of Bromine and Water.

Since β-brompyromucic acid in aqueous solution is readily converted by an excess of bromine into mucobromic acid,[1] it seemed to us of interest to study the behavior of the β-chlorpyromucic acid under the same conditions, since a product containing bromine and chlorine might then be formed. The acid was therefore suspended in five times its weight of water, and an excess of bromine at once added. After heating for a short time, a clear nearly colorless solution was obtained, which was concentrated by evaporation on the water-bath. On cooling, the solution deposited a crystalline acid which was readily soluble in hot water or hot benzol, and but sparingly soluble in these solvents in the cold. The acid recrystallised from water formed thin rhombic plates which melted at 120°–121°, but this melting point could easily be raised to 121°–122° by recrystallisation from benzol.

An analysis of the substance dried over sulphuric acid showed that it was the mucochlorbromic acid whose formation we had been led to expect.

0.2871 gram substance gave 0.4486 gram AgCl + AgBr.

	Calculated for $C_4H_2BrClO_3$.	Found.
Br + Cl	54.11	54.45

The reaction was then precisely analogous to that by means of which mucobromic acid was formed from β-brompyromucic acid:

$$C_5H_3ClO_3 + 3Br_2 + 2H_2O = C_4H_2BrClO_3 + CO_2 + 5HBr.$$

With the material which for the moment was at our disposal, we were unable to study the decomposition of the mucochlorbromic acid by alkalies. We shall hope in the future to prepare in this way a chlorbromacrylic acid, and compare it with the acid of the same composition already described by Mabery and Lloyd.[2]

[1] Proc. Am. Acad. **21**, 152. [2] This Journal 3, 127; and Proc. Am. Acad. **16**, 238.

βγ-Dichlorpyromucic Acid.

Hill and Sanger[1] had shown that in the decomposition of pyromucic tetrabromide or of ethyl pyromucic tetrabromide by alcoholic sodic hydrate, two isomeric dibrompyromucic acids are formed in not widely unequal quantities. There was, therefore, every reason to expect that two isomeric dichlorpyromucic acids could be found in the product formed in a similar way from ethyl pyromucic tetrachloride. Since we had found that a low temperature was essential to the preparation of a pure product, we allowed the ethyl pyromucate to absorb chlorine at 0° until a constant weight was reached, expelled the excess of chlorine by a current of dry air, and decomposed the product at once with an excess of an alcoholic solution of sodic hydrate. The best results were obtained when the tetrachloride was slowly added to a concentrated sodic hydrate solution, taking care to keep the mixture cold.

The sodium salts formed are sparingly soluble in alcohol, and after a short time can be removed by filtration. The alcoholic solution was freed from the excess of sodic hydrate by means of carbonic dioxide, and, after removing the sodic carbonate by filtration, distilled. The sodium salts left on distillation appeared to be identical with those already obtained and were therefore added to the main portion. The alcoholic distillate grew turbid when mixed with water, and gradually deposited a small quantity of a colorless oil which had a peculiar aromatic odor. The quantity of this oil was so small that no investigation of it has as yet been made.

The sodium salt which was obtained from the tetrachloride was dried, dissolved in hot water, and acidified with hydrochloric acid. In this way an acid was obtained which crystallised in finely felted needles, which usually melt at 155°. After two recrystallisations from benzol the acid melted at 168°–169°, and further recrystallisations failed to raise this melting point. Analysis showed this acid to be a dichlorpyromucic acid.

I. 0.4235 gram substance gave 0.5135 gram CO_2 and 0.0455 gram H_2O.

II. 0.2332 gram substance gave 0.3695 gram AgCl.

III. 0.2195 gram substance gave 0.3490 gram AgCl.

	Calculated for $C_5H_2Cl_2O_3$.	Found. I.	II.	III.
C	33.15	33.07	...	...
H	1.10	1.19	...	...
Cl	39.22	...	39.16	39.31

[1] Proc. Am. Acad. 21, 156.

The acid, which proved on subsequent investigation to be the $\beta\gamma^{\alpha}$-dichlorpyromucic acid, is sparingly soluble in cold water, readily in hot, and crystallises as the solution cools in finely felted needles. It is readily soluble in alcohol, ether, or in hot benzol; in cold benzol it is sparingly soluble and crystallises from it in short prisms. In hot chloroform it is also readily soluble, sparingly soluble in the cold. The ready purification of this acid by recrystallisation rendered it improbable that any sensible amount of an isomeric acid was formed with it. The most patient search has failed to show the formation of such a product in appreciable quantity, and from pure ethyl pyromucic tetrachloride almost pure $\beta\gamma$-dichlorpyromucic acid is obtained at once. The yield of pure acid ordinarily obtained from pyromucic ether is not wholly satisfactory, since it amounts to about 50 per cent. of the weight of ether taken, or about 39 per cent. of the theoretical amount.

The solubility of the acid in cold water we determined as usual. A weighed quantity of a solution of the acid saturated at 19.5° was boiled with baric carbonate and the barium dissolved precipitated by sulphuric acid.

I. 36.2505 grams solution saturated at 19.5° gave 0.0619 gram $BaSO_4$.

II. 35.6546 grams solution saturated at 19.5° gave 0.0615 gram $BaSO_4$.

According to these determinations, the solution saturated at 19.5° contains the following percentages of acid:

I.	II.
0.27	0.27

Baric $\beta\gamma$-dichlorpyromucate, $Ba(C_5HCl_2O_3).3H_2O$.[1] — The barium salt may be most conveniently prepared by precipitating a

[1] We have already referred to the brief description of the $\beta\gamma$-dichlorpyromucic acid published by Denaro in the Gazzetta Chimica (**16**, 333), and have asserted that the analyses of the two salts which he describes are not worthy of confidence. In support of our assertion we append his results in full, together with the analytical data upon which they depend. The errors in the calculated percentages are corrected in parenthesis.

Barium salt:

0.4480 gram of the salt lost at 110° 0.00204 gram H_2O.

	Calculated for $Ba(C_5HCl_2O_3)_2.3H_2O$.	Found.
H_2O	9.80	8.30 (0.445)

0.1939 gram of the dry salt gave 0.0769 gram $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2$.	Found.
Ba	23.54 (27.56)	23.32

solution of the ammonium salt with baric chloride. It is rather sparingly soluble even in hot water, and still less soluble in cold water. It separates from a hot concentrated solution in fine clustered needles which contain three molecules of water. The crystals are permanent in the air, but lose their water readily at 100°.

I. 1.2048 gram air-dried salt lost at 100° 0.1170 gram H_2O.

II. 1.2118 gram air-dried salt lost at 100° 0.1132 gram H_2O.

III. 0.5694 gram air-dried salt gave 0.2393 gram $BaSO_4$.

IV. 0.3783 gram air-dried salt gave 0.1593 gram $BaSO_4$.

	Calculated for $Ba(C_5HCl_4O_3)_2.3H_2O$.	Found. I.	II.	III.	IV.
H_2O	9.80	9.71	9.34	...	...
Ba	24.86	...	...	24.71	24.76

I. 0.4828 gram salt dried at 100° gave 0.2250 gram $BaSO_4$.

II. 0.5540 gram salt dried at 100° gave 0.2579 gram $BaSO_4$.

	Calculated for $Ba(C_5HCl_4O_3)_2$.	Found. I.	II.
Ba	27.56	27.40	27.36

The solubility of the salt in water at 19.5° was determined according to the method of V. Meyer.

I. 23.0222 grams solution saturated at 19.5° gave 0.0503 gram $BaSO_4$.

II. 22.4890 grams solution saturated at 19.5° gave 0.0487 gram $BaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
0.46	0.46

Calcic βγ-dichlorpyromucate, $Ca(C_5HCl_2O_3)_2.4H_2O$.—The calcium salt was prepared by boiling a solution of the acid with an

---

Calcium salt:

0.6942 gram of the salt lost at 110° 0.0300 gram H_2O.

	Calculated for $Ca(C_5HCl_2O_3)_2.3\frac{1}{2}H_2O$.	Found.
H_2O	13.60	14.45 (4 32)

0.3024 gram of the salt gave 0.1072 gram $CaSO_4$.

	Calculated for $Ca(C_5HCl_2O_3)_2$.	Found.
Ca	10.00	10.42

These results can hardly be explained unless it is assumed that they contain both typographical and arithmetical errors. The two remaining analyses contained in Denaro's paper, two chlorine determinations in the free acid, are correctly calculated and agree well with the theory.

excess of calcic carbonate. It is readily soluble in hot water, less soluble in cold, and crystallises from a hot concentrated solution in long clustered needles which contain four molecules of water.

The crystallised salt is permanent in the air, effloresces slowly over sulphuric acid, and loses all its water readily at 110°.

I. 2.7640 grams air-dried salt lost at 110° 0.4160 gram H_2O.

II. 3.1275 grams air-dried salt lost at 113° 0.4707 gram H_2O.

	Calculated for $Ca(C_4HCl_2O_3)_2.4H_2O$.	Found. I.	II.
H_2O	15.26	15.05	15.05

I. 0.6595 gram salt dried at 110° gave 0.2227 gram $CaSO_4$.

II. 0.7004 gram salt dried at 113° gave 0.2366 gram $CaSO_4$.

	Calculated for $Ca(C_4HCl_2O_3)_2$.	Found. I.	II.
Ca	10.00	9.93	9.94

The solubility of the salt in water at 19.5° was determined as usual. The calcium was precipitated as oxalate and the oxalate ignited with sulphuric acid.

I. 22.8797 grams solution saturated at 19.5° gave 0.0944 gram $CaSO_4$.

II. 21.5915 grams solution saturated at 19.5° gave 0.0891 gram $CaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
1.21	1.21

Potassic βγ-dichlorpyromucate, $KC_5HCl_2O_3$.—The potassium salt is readily soluble in hot water, but rather sparingly soluble in cold water, and separates from a hot concentrated solution in small prisms which are anhydrous.

I. 0.6130 gram substance dried at 120° gave 0.2435 gram K_2SO_4.

II. 0.8200 gram substance dried at 120° gave 0.3265 gram K_2SO_4.

	Calculated for $KC_5HCl_2O_3$.	Found. I.	II.
K	17.84	17.83	17.87

Argentic βγ-dichlorpyromucate, $AgC_5HCl_2O_3$.—If argentic nitrate is added to a cold aqueous solution of the acid, the silver salt is precipitated in the form of fine needles. For analysis we

prepared the salt by precipitating a dilute neutral solution of the ammonium salt with argentic nitrate, and recrystallising the precipitated salt from hot water. It is sparingly soluble even in hot water, and separates on cooling the hot saturated solution in fine needles.

I. 0.3230 gram substance dried over H_2SO_4 gave 0.1612 gram AgCl.

II. 0.2580 gram substance dried over H_2SO_4 gave 0.1282 gram AgCl.

	Calculated for $AgC_5HCl_2O_3$.	Found. I.	II.
Ag	37.50	37.57	37.41

Ethyl βγ-dichlorpyromucate, $C_5HCl_2O_3C_2H_5$.—The ethyl ether was prepared by heating at 100° for three hours a mixture of five parts of acid, eight parts of absolute alcohol, and five parts of concentrated sulphuric acid (sp. gr. 1.84). It was precipitated with water, washed with dilute sodic carbonate, and then with water. It is readily soluble in hot alcohol, more sparingly in cold, and crystallises in large needles which melt at 63°–64°.

I. 0.2645 gram substance dried over H_2SO_4 gave 0.3640 gram AgCl.

II. 0.1933 gram substance dried over H_2SO_4 gave 0.2673 gram AgCl.

	Calculated for $C_5HCl_2O_3C_2H_5$.	Found. I.	II.
Cl	33.98	34.02	34.18

βγ-Dichlorpyromucamide, $C_5HCl_2O_2NH_2$.—The ethyl ether of βγ-dichlorpyromucic acid is readily attacked by strong aqueous ammonia even in the cold, and in a short time is converted into the amide. The amide is sparingly soluble even in hot water, and crystallises in long slender needles which melt at 176°–177°.

0.4015 gram substance dried over H_2SO_4 gave 28.5 cc. moist N at 23° under a pressure of 767 mm.

	Calculated for $C_5HCl_2O_2NH_2$.	Found.
N	7.78	8.03

The formation of but one dichlorpyromucic acid in the decomposition of the ethyl pyromucic tetrachloride by alkalies, while two isomeric acids are always obtained under the same circumstances from the corresponding bromine compound, made it impossible to predict its constitution from the method of formation. Still, its

comparatively high melting point, its physical properties, and the ready solubility of its calcium salt, in which it closely resembles the $\beta\gamma$-dibrompyromucic acid, gave fair ground for the conjecture that it had a similar structure. A study of its oxidation products showed that such was the case, since we easily obtained from it mucochloric and dichlormaleic acids.

Action of Bromine and Water.

If bromine is added to $\beta\gamma$-dichlorpyromucic acid suspended in six or eight times its weight of cold water, oxidation rapidly ensues, with the escape of carbonic dioxide. A slight excess of bromine was added, and the reaction completed by the aid of heat. On cooling, the solution solidified with the separation of colorless crystals, which when recrystallised from water and finally from benzol melted at 124°–125°, and had the characteristic form of mucochloric acid. Analysis also gave the proper percentage of chlorine.

I. 0.2015 gram substance dried over H_2SO_4 gave 0.3408 gram AgCl.

II. 0.2320 gram substance dried over H_2SO_4 gave 0.3922 gram AgCl.

	Calculated for $C_4H_2Cl_2O_3$.	Found. I.	II.
Cl	42.01	41.81	41.79

In this case the reaction may be represented by the equation

$$C_5H_3Cl_3O_3 + 2Br_2 + 2H_2O = C_4H_3Cl_2O_3 + CO_2 + 4HBr.$$

Action of Nitric Acid.

Nitric acid acts but slowly upon the $\beta\gamma$-dichlorpyromucic acid, and for its complete oxidation we have found it necessary to take for one part of the acid 3 parts of concentrated nitric acid (sp. gr. 1.42) diluted with twice its weight of water. After boiling for five hours the action appeared to be complete, and as the clear solution deposited nothing on cooling, we extracted it with ether. The ether left upon evaporation a colorless crystalline mass, which proved to be a mixture of two substances, one readily soluble, the other but sparingly soluble in cold water. The sparingly soluble substance, when recrystallised from hot water, was recognised by its crystalline form and by its melting point, 124°–125°, as mucochloric acid. The acid, which was readily soluble in cold water,

was neutralised with baric carbonate, the barium salt precipitated from its aqueous solution by alcohol, and the acid liberated from this purified barium salt again extracted with ether. The crystalline acid left by the evaporation of the ether was then dissolved in a small amount of water, and on standing, well formed rhombic plates separated, which were dried over sulphuric acid for analysis.

0.2233 gram substance gave 0.3433 gram AgCl.

	Calculated for $C_4H_2Cl_2O_4$.	Found.
Cl	38.38	38.01

The identity of this acid with dichlormaleic acid was further determined by the melting point of the anhydride prepared by sublimation, which we found to be 119°–120°, in agreement with the statement of Ciamician and Silber.[1]

The oxidation therefore took place in accordance with the following reactions,

$$C_5H_3Cl_2O_2 + 2O = C_4H_2Cl_2O_2 + CO_2,$$
$$C_5H_3Cl_2O_2 + 3O = C_4H_2Cl_2O_4 + CO_2,$$

and the dichlorpyromucic acid in question is thus conclusively shown to have its chlorine atoms in the β and γ positions.

Preparation of Isomeric Dichlorpyromucic Acids.

Although we had been unable to find the $\beta\delta$-dichlorpyromucic acid among the products formed by the action of alkalies upon ethyl pyromucic tetrachloride, it seemed to us probable that it might be formed under the proper conditions by the direct action of chlorine upon ethyl pyromucate, or by the decomposition of its tetrachloride by heat alone.

Tönnies[2] had already shown that δ-brompyromucic acid could be formed by heating pyromucic tetrabromide, and Hill and Sanger[3] had further shown that δ-brompyromucic acid and $\beta\delta$-dibrompyromucic acid could conveniently be made by the action of bromine upon pyromucic acid at high temperature. As subsequent experiments in this laboratory had shown that these two acids could more advantageously be made by substituting the ethyl ether for the acid, and our own experiments had shown that the δ-chlorpyromucic acid could readily be made in this way, we proceeded to study the action of chlorine upon ethyl pyromucate

[1] Ber. d. chem. Ges. **16**, 2396. [2] Ibid. **11**, 1088. [3] Proc. Am. Acad. **21**, 135, 160.

at high temperature. It seems hardly necessary to describe in detail the numerous experiments which we made under widely varying conditions, each one of which yielded us purely negative results. Ethyl pyromucate was treated with chlorine at temperatures ranging from 145° to its boiling point, both by itself and after the addition of iodine or aluminic chloride, but in no case was the desired product obtained. Pyromucic acid and δ-chlorpyromucic acid also failed to give such a product when treated at high temperatures with chlorine, and we were equally unsuccessful when we used the chloranhydrides of these acids either with or without an excess of phosphoric pentachloride. We then studied the action of heat upon the tetrachloride of pyromucic acid itself, of its chloranhydride and ethyl ether, and of the ethyl ether of δ-chlorpyromucic acid, and found in each case that small quantities of a dichlorpyromucic acid were formed which closely resembled the $\beta\delta$-dibrompyromucic. A more careful investigation further proved that in the decomposition of the ethyl pyromucic tetrachloride a second new dichlorpyromucic acid was formed concerning whose constitution we are not yet able to speak definitely. This acid we propose to call the χ-dichlorpyromucic acid until its structure is established. The amount of the dichlorpyromucic acids which we have been able to obtain is but small, and we have made many unsuccessful attempts to increase the yield by varying the temperature or the mode of heating, or by adding iodine, or aluminic or ferric chloride, before heating.

We first obtained the $\beta\delta$-dichlorpyromucic acid by distilling under ordinary pressure the product formed by treating pyromucic acid with chlorine at 100°. Hydrochloric acid is given off in quantity, and, although a large carbonaceous residue is left in the retort, a liquid distillate is obtained which, after repeated distillation through a Hempel's column, amounts to about 85 per cent. of the weight of the pyromucic acid taken and then distills, leaving but an insignificent carbonaceous residue. This distillate is extremely complex in its nature, and we have as yet made no thorough study of its constituents. We found, however, that the portions which boiled between 196° and 220° gave considerable quantities of $\beta\delta$-dichlorpyromucic acid when treated with cold water. They therefore contained the corresponding chloranhydride of the acid. The yield thus obtained amounted to but about 4 per cent. of the pyromucic acid taken. From ethyl pyromucic

tetrachloride we succeeded in obtaining a somewhat better yield. We found it advantageous to purify the tetrachloride by one distillation *in vacuo*, and to distill the product thus obtained under ordinary pressure. More or less carbonisation ensued, and on fractional distillation *in vacuo* through a Hempel's column[1] the distillate was found to contain considerable unaltered tetrachloride. That portion which boiled above 140° under 16 mm. pressure was therefore redistilled under ordinary pressure and the distillate again fractioned *in vacuo*. After repeated distillations we found that the portion which boiled between 118° and 123° under 16 mm. pressure partially solidified on cooling, and that a few crystals were also formed in the next lower fraction. These fractions were therefore strongly cooled and the crystalline solid removed by filtration and the liquid portions further distilled. The solid thus obtained proved to be the ethyl ether of the new χ-dichlorpyromucic acid melting at 197°–198°, which we shall presently describe. When no more of this crystalline ether could be obtained by cooling, the liquid fractions were saponified by alcoholic sodic hydrate, the acids liberated by hydrochloric acid and separated through their calcium and barium salts. From the fraction boiling below 110° (16 mm.) we obtained chiefly δ-chlorpyromucic acid melting at 176°–177°, although it yielded also a small quantity of $\beta\delta$-dichlorpyromucic acid, which was readily isolated by means of its sparingly soluble barium salt. The fractions 110°–118° and 118°–123° apparently consisted chiefly of the ethyl ether of $\beta\delta$-dichlorpyromucic acid, but the latter necessarily contained also a small amount of the crystalline ethyl χ-dichlorpyromucate held in solution. The two dichlorpyromucic acids could readily be separated through the different solubilities of their calcium salts, the calcic $\beta\delta$-dichlorpyromucate like the calcium salt of the corresponding bromine derivative being very

[1] For fractional distillation under diminished pressure we used the extremely convenient apparatus of Anschütz. We found that the ease of separation could be materially increased by filling a few inches of the stem of the distilling flask with glass beads, and thus combining the Hempel's column with the vacuum distillation. The beads were supported upon a perforated disk of platinum foil slipped over the capillary air tube and held in place by a slight enlargement of the tube. The thermometer was then raised to the proper line by a short bit of small glass tubing dropped into the air tube. Hantzsch (Ann. Chem. (Liebig) **249**, 57) has used with advantage for distillation under ordinary pressure a long necked boiling flask whose stem is partially filled with beads supported upon a platinum foil forced into the neck. We have for a long time used such a Hempel's column, but have supported the beads conveniently upon a glass bulb which nearly fills the stem and whose sealed neck is long enough to rest upon the bottom of the flask.

sparingly soluble in water. From 123°–130° but an insignificant fraction was collected, and the fraction 130°–153° consisted in part at least of unaltered ethyl pyromucic tetrachloride, from which $\beta\gamma$-dichlorpyromucic acid was obtained.

100 grams of ethyl pyromucate yielded us 197 grams of the tetrachloride, and from this we obtained the following weights of pure products:

5.0 grams δ-chlorpyromucic acid.
12.2 grams $\beta\gamma$-dichlorpyromucic acid.
2.7 grams χ-dichlorpyromucic acid.
16.1 grams ethyl χ-dichlorpyromucate.

If pyromucyl chloride is treated with chlorine at 0°, the chlorine is absorbed very slowly, but the gain in weight finally approximately corresponds with that required for the formation of a tetrachloride. If the tetrachloride is distilled under ordinary pressure, only an inconsiderable carbonaceous residue is left in the retort, and after repeated distillations through a Hempel's column under ordinary pressure a product is obtained which, when treated with water, yields the $\beta\delta$-dichlorpyromucic acid and the χ-dichlorpyromucic acid. While the yield of the $\beta\delta$-dichlorpyromucic acid thus obtained is somewhat greater than that obtained from the ethyl pyromucic tetrachloride, the yield of the χ-dichlorpyromucic acid is much smaller.

By treating ethyl δ-chlorpyromucate in the cold with chlorine, and distilling the addition product thus formed under ordinary pressure, we also obtained the $\beta\delta$-dichlorpyromucic acid. While the yield was somewhat larger than that obtained from the ethyl pyromucic tetrachloride, it did not repay us for the loss of time and material involved in making the δ-chlorpyromucic acid. Moreover, to our surprise, we could obtain in this way none of the crystalline ethyl χ-dichlorpyromucate.

$\beta\delta$-Dichlorpyromucic Acid.

The acid whose preparation has just been described can most readily be purified by repeated precipitation from ammoniacal solution with calcic chloride, and recrystallisation from chloroform. The acid thus purified gave on analysis the following results:

I. 0.2577 gram substance gave 0.3129 gram CO_2 and 0.0259 gram H_2O.

II. 0.1933 gram substance gave 0.3053 gram AgCl.

	Calculated for $C_5H_3ClO_3$.	Found. I.	II.
C	33.15	33.11	...
H	1.10	1.12	...
Cl	39.22	...	39.04

βδ-Dichlorpyromucic acid is readily soluble in ether or alcohol. It dissolves readily in hot water, benzol, or chloroform, and the greater part of the acid is in each case deposited on cooling in oblique prisms, which are frequently twinned in forms which can hardly be distinguished from those of the *βδ*-dibrompyromucic acid. The acid melts sharply at 155°–156°, and sublimes unaltered at a higher temperature.

The solubility of the acid in water at 19.5° was determined in the usual manner. A weighed quantity of a solution of the acid saturated at 19.5° was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid.

I. 42.8007 grams solution saturated at 19.5° gave 0.0724 gram $BaSO_4$.

II. 51.4109 grams solution saturated at 19.5° gave 0.0907 gram $BaSO_4$.

According to these determinations, the solution saturated at 19.5° contained the following percentages of acid:

I.	II.
0.26	0.27

Baric βδ-dichlorpyromucate, $Ba(C_5HCl_2O_3)_2.4H_2O$.—The barium salt was prepared by precipitating a dilute solution of the ammonium salt with baric chloride, and recrystallising the product thus obtained from water. The salt is sparingly soluble in hot water, still less soluble in cold water, and crystallises from a hot concentrated solution in long irregular flat prisms which contain four molecules of water.

The salt is permanent in the air, effloresces over sulphuric acid, and loses its water readily at 100°.

I. 1.4513 gram air-dried salt lost at 100° 0.1795 gram H_2O.

II. 0.4908 gram air-dried salt gave 0.1981 gram $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2.4H_2O$.	Found. I.	II.
H_2O	12.66	12.37	...
Ba	24.07	...	23.73

0.4751 gram salt dried at 100° gave 0.2205 gram $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2$.	Found.
Ba	27.56	27.29

The solubility of the salt in water at 19.5° was determined in the usual manner.

I. 28.4671 grams solution saturated at 19.5° gave 0.0561 gram $BaSO_4$.

II. 28.6844 grams solution saturated at 19.5° gave 0.0573 gram $BaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
0.42	0.43

Calcic βδ-dichlorpyromucate, $Ca(C_5HCl_2O_3)_2.3H_2O$.—The calcium salt was prepared by precipitating a dilute solution of the ammonium salt with calcic chloride, and recrystallising the product from hot water. It is but sparingly soluble in hot water, still less soluble in cold water, and separates from a hot concentrated solution in flattened prisms with rectangular terminations. The crystallised salt is permanent in the air, effloresces slowly over sulphuric acid and loses all its water at 125°.

I. 1.5490 gram air-dried salt lost at 125° 0.1820 gram H_2O.

II. 0.4067 gram air-dried salt gave 0.1219 gram $CaSO_4$.

	Calculated for $Ca(C_5HCl_2O_3)_2.3H_2O$.	Found. I.	II.
H_2O	11.90	11.75	...
Ca	8.81	...	8.81

0.6899 gram salt dried at 125° gave 0.2332 gram $CaSO_4$.

	Calculated for $Ca(C_5HCl_2O_3)_2$.	Found.
Ca	10.00	9.94

The solubility of the salt in water at 19.5° was determined in the usual manner. The calcium was precipitated as oxalate and ignited with sulphuric acid.

I. 32.1733 grams solution saturated at 19.5° gave 0.0244 gram $CaSO_4$.

II. 36.7555 grams solution saturated at 19.5° gave 0.0289 gram $CaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
0.22	0.23

Ethyl βδ-dichlorpyromucate, $C_5HCl_2O_3C_2H_5$.—The ethyl ether was prepared by the action of ethyl iodide on the silver salt, and is a heavy liquid of pleasant odor. It melts at 2°–3°, and distills at 116°–118° under a pressure of 16 mm., the oil-bath being at 165°–175°. An analysis of the distilled ether gave the following result:

0.2157 gram substance gave 0.2957 gram AgCl.

	Calculated for $C_5HCl_2O_3C_2H_5$.	Found.
Cl	33.98	33.89

βδ-Dichlorpyromucamide, $C_5HCl_2O_2NH_2$.—The ethyl ether is but slowly attacked by concentrated ammonia in the cold, but at 100° it is readily converted to the amide. The amide is sparingly soluble in cold water, more readily in hot, and separates from a hot concentrated solution in long needles, which on standing are converted into oblique prisms which melt at 153°–154°.

0.2781 gram substance dried over H_2SO_4 gave 20.0 cc. moist N at 25.5° under a pressure of 766 mm.

	Calculated for $C_5HCl_2O_2NH_2$.	Found.
N	7.78	8.06

Although the melting point, the crystalline form, and the insolubility of its calcium salt showed that this acid closely resembled the βδ-dibrompyromucic acid, it was evidently necessary to establish the position of the chlorine atoms by means of its oxidation products.

Action of Bromine and Water.

Hill and Sanger[1] found that the βδ-dibrompyromucic acid was readily attacked by aqueous bromine in the cold with the formation of monobrommaleyl bromide. The βδ-dichlorpyromucic acid is but slowly attacked by aqueous bromine in the cold, and we therefore suspended it in five times its weight of water, added at once somewhat more than four atoms of bromine, heated until the oil which was first formed had almost all disappeared, and evaporated the solution at a gentle heat. The crystalline mass thus obtained was readily soluble even in cold water, and very sparingly soluble even in hot chloroform or benzol. The product was dissolved in cold water, filtered, and evaporated nearly to dryness.

[1] Proc. Am. Acad. **21**, 165.

The crystals which separated were pressed dry with filter paper, washed carefully with hot benzol, and recrystallised from a little hot water. The acid thus prepared crystallised in microscopic crystals which melted at 189°–190°,[1] and proved on analysis to contain the percentage of chlorine required by monochlorfumaric acid.

0.1288 gram substance dried over H_2SO_4 gave 0.1227 gram AgCl.

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.59	23.55

The oxidation with bromine and water therefore takes place in accordance with the following equation:

$$C_5H_3Cl_2O_2 + 2Br_2 + 3H_2O = C_4H_3ClO_4 + CO_2 + HCl + 4HBr.$$

Since the $\beta\delta$-dichlorpyromucic is but slowly attacked even by concentrated nitric acid, it was not thought worth while to study the reaction in detail.

[*To be continued.*]

ON THE PRESENCE OF SUGAR-YIELDING INSOLUBLE[2] CARBOHYDRATES IN SEEDS.

By W. Maxwell.

In the physiological study of seeds and plants, and in the chemical analysis of their known constituents, anything like an even approximate determination of the sum and character of those constituents has not been made, research having been pursued within limits which have acknowledged a large percentage residue of "undetermined matter." These undetermined matters, excluding nitrogenous substances whose nature is not fully understood, have been summarily expressed as nitrogen-free extract matter (N-freie Extractstoffe).

It has not appeared probable that this large proportion of the total constituent matters of seeds is incapable of a chemically expressible composition, and without a definite function in the life

[1] Kauder (J. prakt. Chem. [2], **31**, 28) gives the melting point as 191°.

[2] Insoluble in water and diastase.

and development of the plant; and, further, that those matters can only act a negative part in the appropriation of vegetable substances by the animal system. These considerations have led to investigation.

In the course of researches conducted by Prof. E. Schulze and Dr. E. Steiger[1] with the seeds of Lupinus luteus, the non-nitrogenous matter of those seeds, after the separation and study of the soluble carbohydrates by Dr. Steiger,[2] was found to contain an insoluble carbohydrate which, by treatment with a dilute mineral acid, yielded a sugar capable of reducing Fehling's solution, and which exhibited all the properties of galactose. This insoluble sugar-yielding body was named Paragalactin, and has the formula of the soluble galactin, $C_6H_{10}O_5$.[3]

The author, during a study of the legumes Pisum sativum, Faba vulgaris, and Vicia sativa, at the instance of Prof. Schulze, and as a part of that special course of research of the Zürich Agricultural Chemical Laboratory, made an investigation of the non-nitrogenous insoluble residues in respect of the presence of sugar-yielding bodies in those seeds.

The method of research was as follows: About one kilo of finely ground material was saturated with ether, for the removal of the fats. The fat-free material was treated with dilute potassium hydrate in order to take out the greater part of the proteid bodies. Pouring off the alkaline extractant and washing with water until neutral, the material was further treated with a solution of diastase for the separation of the amyloids. Having by aid of these several processes removed from the original material the fats, albuminoids, starches, and, of course, all soluble carbohydrates, a residue was left which was composed of cellulose, the remnants of the less soluble albuminous matters, and that large aggregate already expressed as nitrogen-free extract matter. That insoluble residue was boiled with a solution of sulphuric acid of a concentration of 3.5 per cent. for one hour. After filtering, the extraction was diluted with an equal volume of water and further boiled for two hours under a condenser, and afterwards neutralised with barium carbonate and the neutral solution evaporated down to a syrup consistence. The syrup residue was extracted by boiling consecutively with alcohols of respectively 95 and 90 per cent. concentrations. The alcoholic extractions, after further

[1] Ber. d. chem. Gesell. **2**, 1887. [2] Inaugural dissertation, 1887. [3] Ibid.

various treatments to obtain those more pure, were set aside in desiccators for primary crystallisation, or evaporated down and the water solution of the residue studied direct.

As the results obtained in the general investigations show very considerable variations, the properties and data pertaining to each variety of seeds that has been studied will be separately given. This must more particularly be done because the researches, which were to be made with the varieties of legumes already specified, have been extended so as to include a study of other kinds, embracing also representatives of the monocotyledons.

Vicia sativa.

The final alcoholic extraction, obtained, as already described, by boiling the sulphuric acid hydration product of the original non-nitrogenous residue with alcohol, after standing for some eight days in the desiccator, was a half-crystallised, half-syrup mass, which the presence of non-crystallisable bodies made it very difficult to obtain in a pure state.

By adding a few drops of the syrup, or of the water solution of the same, to boiling Fehling's solution, a heavy precipitation of copper oxide occurred, indicating that a reducing sugar was present.

When heated with concentrated nitric acid, mucic acid was obtained as the product of oxidation, having a melting point of 209°–210° C.

In order to observe the action of an aqueous solution of the body upon the ray of polarised light, the sugar contained in a given volume was determined by means of Fehling's solution.

100 cc. of the aqueous solution contained 6.48 per cent. sugar. The value of the rotatory action was calculated according to the formula $[\alpha]_D$.[1]

$$[\alpha]_D = \frac{A \times 0.346 \times 100}{l \times P}$$

$$\alpha = 22.1,$$
$$l = 2.0,$$
$$P = 6.48.$$

$$[\alpha]_D = \frac{22.1 \times 0.346 \times 100}{2 \times 6.48} = \frac{764.66}{12.96} = +59°.$$

[1] Landolt.

If the polarisation value of the body be considered in relation with its reducing action upon Fehling's solution and the formation of mucic acid as an oxidation product, it is indicated that more than one sugar kind is contained in the solution. That galactose is present is proved by the fact that the body yields mucic acid when heated with concentrated nitric acid, that sugar being the only one of the glucoses which gives mucic acid as a product of oxidation. However, as the rotatory power of galactose is 81.5, it is apparent that at least one other sugar is present which operates upon the ray of polarised light to the left. The levo-rotatory influence, with the non-crystallisable property of a large part of the body, suggests the presence of levulan. At present it has not been determined.

Faba vulgaris.

With this variety a more developed crystallisation was obtained from the alcoholic extraction in a form resembling galactose, white crystals partially separating from the syrup upon the sides of the crystallising dish. However, a pure preparation of that sugar was not obtained on account of the considerable mass of attaching syrup.

The properties exhibited by the body were in part similar to those in the example of Vicia sativa.

Fehling's solution was powerfully reduced.

A large amount of mucic acid was obtained by heating the body with concentrated nitric acid, with a melting point of 208°–209° C.

The value of polarisation was + 78.3

In the example of Faba vulgaris, the reducing of a copper solution and the large yield of mucic acid by treatment of the body with nitric acid not only demonstrate the presence of galactose; the high reading of the rotatory action of the aqueous solution of the sugar indicates that the insoluble carbohydrate present in the non-nitrogenous matter of those seeds is, in most part, convertible into galactose.

Pisum sativum.

The alcoholic extraction did not stand to allow of the possibility of getting crystallised sugars; it was directly examined in respect of its properties.

The reducing of Fehling's solution and the yielding of mucic acid when heated with concentrated nitric acid were as characteristic as in the foregoing examples.

An aqueous solution of the syrup which contained 9.5 grams of sugar in 100 cc., according to the formula $[\alpha]_D$, showed a dextro-rotatory reading of +80.0.

It thus is indicated that the seeds of Pisum sativum contain an insoluble carbohydrate which, upon treatment with a dilute mineral acid, yields an inversion product which is wholly galactose. That insoluble carbohydrate *must be paragalactin*.

In addition to the investigation of those legumes, research was conducted with certain representatives of the monocotyledons, in order to observe if those insoluble carbohydrates were more generally distributed through vegetable organisms.

A portion of the cattle food prepared from the cocoa seed (Palmacea) was treated the same as the examples already given. The final alcoholic extraction which had been evaporated to a syrup, after standing some weeks in a desiccator, was a half-crystallised, half-syrup mass, and the crystallisation could not be further induced by treatments with alcohol in vacuum.

The syrup reduced Fehling's solution, and, upon treatment with concentrated nitric acid at a moderate heat, a large yield of mucic acid was given.

An aqueous solution of the body, containing 10.314 grams in 100 cc., gave a dextro-rotatory reading, according to the given formula, of +81.0°. It appears that the given specimen of Palmacea contains the galactose-yielding carbohydrate present in Pisum sativum, which is indicated by the same optical and chemical properties. In one other representative of the Palmacea, the palm nut, the inversion product of the non-nitrogenous insoluble matter agreed chemically in its properties with the cocoa-nut. The action of its aqueous solution upon the ray of polarised light was very different; it gave a reading of + 29.8°.

The latter example shows the properties peculiar to the alcoholic extract obtained in the case of Vicia sativa. The presence of galactose in the non-crystallisable syrup was demonstrated by oxidising with nitric acid, which gave a formation of mucic acid. The low dextro-reading of the polariscope, however, indicates that a considerable proportion of some sugar is present, rotating the polarised ray to the left. That sugar may be levulose, which is indicated by the non-crystallisable property of the syrup and by its optical behavior. If levulose were the sugar present, it must be in a less proportion than the galactose, otherwise the dextro-

rotatory action of the latter body had been further neutralised by the comparatively greater negative operation of the levulose.

The researches were further extended to coffee berries and soja beans. The alcoholic syrup extracts obtained from the inverted non-nitrogenous residues of those seeds, in addition to exhibiting the chemical and optical properties peculiar to the previous examples treated of, yielded large crystallised preparations of galactose sugar. By recrystallising several times out of alcohol, chemically pure preparations were obtained. Aqueous solutions of the sugar were prepared, containing 10 grams in 100 cc., the sugar having been previously dried at 100° C. The solutions were brought into the observation tube at a temperature of 17° C.

The rotatory powers of the sugars obtained from the respective seeds were as follow:

Soja beans $= +81.3$
Coffee berries $= +81.1$

The rotatory values assigned to galactose prepared from milk sugar by the given authorities are:

Meisel[1] $= +81.53$,
Scheibler[2] $= +81.2$,
Tollens[3] $= +81.40$

Upon resuming the study of the legumes at the Harvard College Laboratory, the author investigated the seeds of Phaseolus vulgaris, and with a similar result in respect of the presence of at least one insoluble carbohydrate, which by treatment with dilute sulphuric acid was converted into galactose. Paragalactin appears thus to be present in the insoluble non-nitrogenous matters of the "Boston bean."

It having been demonstrated that the insoluble non-nitrogenous matters of certain seeds contain sugar-yielding bodies, and that those carbohydrates appear, in some representatives, to form almost the whole of the non-nitrogenous substance, excluding cellulose, it became desirable to obtain a quantitative estimation of the relative amounts of those carbohydrates contained in the respective varieties of the legumes under investigation.

To that end a method of estimation was adopted based upon the principle of the previous separation of the fats, soluble carbohydrates, starch, and the chief part of the albuminoids. The

[1] J. prakt. Chem. **22**, 100. [2] Ber. d. chem. Gesell. **17**, 1731. [3] Ibid. **17**, 678.

nitrogen still contained in the residue was determined and calculated as representing unremoved proteids. The proteids, with the cellulose and any remnant of mineral matter, were deducted from the amount of the residue, and the remainder was accepted, by difference, as expressing the percentage of insoluble carbohydrates.

A second and direct method of estimating approximately the amount of those bodies was by inversion of a given weight of the residue with hydrochloric acid, allowing, as by the previous method, for the sum of proteids and cellulose, and determining the sugar of the inversion product by means of Fehling's solution gravimetrically.

Estimations were made of the quantitative amounts of those bodies in the representatives of legumes already qualitatively treated of.

Pisum sativum.

The mean of two determinations showed that the nitrogen contained in residue, obtained according to the method described, was = 6.147 per cent. That amount, when multiplied by the nitrogen factor[1] of the albuminoids present in legumes, gives:

$$6.147 \times 5.75 = 35.34 \text{ per cent. proteids,}$$
$$14.64 \quad \text{“} \quad \text{cellulose.}$$
$$49.98 \quad \text{“}$$

Amount of insoluble carbohydrates in the residue, 50.02 per cent.; calculated from the original material, 20.02 per cent.

The result of the estimation of those bodies by direct inversion of the residue was as follows:

7.794 grs. res. (18.949 grs. orig. mat.) = 3.888 grs. sugar,
= 3.499 grs. carbohydrate,
= 18.46 per cent.

Between the estimation by difference and by direct inversion a variation of only 1.5 per cent. occurred, indicating that practically the whole of the insoluble non-nitrogenous matters present in the seeds of Pisum sativum is convertible into a sugar which was previously seen to be galactose, the hydration product of paragalactin.

[1] Ritthausen: Die Eiweissstoffe der Getreidearten und Hülsenfrüchte.

Faba vulgaris.

The mean of two determinations of nitrogen present in the residue was 8.587 per cent.

$$8.587 \times 5.75 = 49.37 \text{ per cent. proteids,}$$
$$16.79 \quad \text{“} \quad \text{cellulose.}$$
$$66.16 \quad \text{“}$$

Insoluble carbohydrates in residue, 33.83 per cent.; calculated from original material, 14.41 per cent.

Determination by direct inversion:

6.092 grs. res. (14.298 grs. orig. mat.) = 1.083 grs. sugar,
= 0.975 gr. carbohydrate,
= 6.819 per cent.

In the example of Faba vulgaris only about one half of the residue matter, indicated by the “difference” method as being insoluble carbohydrate, was convertible into sugars. The remaining portion will be further investigated.

Vicia sativa.

Two nitrogen determinations gave a mean of 8.984 per cent.

$$8.984 \times 5.75 = 51.628 \text{ per cent. proteids,}$$
$$11.182 \quad \text{“} \quad \text{cellulose.}$$
$$62.84 \quad \text{“}$$

Insoluble carbohydrates in residue, 37.16 per cent.; calculated from original material, 15.162 per cent.

Determination by direct inversion:

7.457 grs. res. (16.785 grs. orig. mat.) = 1.372 grs. sugar,
= 1.234 grs. carbohydrate,
= 7.36 per cent.

Those quantitative data show a close resemblance to the results obtained in the example of Faba vulgaris.

Phaseolus vulgaris.

The mean of two nitrogen determinations was 3.425 per cent.

$$3.425 \times 5.75 = 19.693 \text{ per cent. proteids,}$$
$$21.770 \quad \text{“} \quad \text{cellulose.}$$
$$41.463 \quad \text{“}$$

Insoluble carbohydrate in residue, 58.537 per cent.; calculated as original material, 8.2 per cent.

Determination by direct inversion:

3.524 grs. res. (25.27 grs. orig. mat.) = 2.026 grs. sugar,
= 1.8 grs. carbohydrates,
= 7.12 per cent.

In recapitulating the results of the investigations and the data which have been obtained in relation to those examples of legumes and of other seed kinds that have been under consideration, it appears to have been established that the insoluble non-nitrogenous matters, exclusive of cellulose, contained in the seeds of certain vegetable species are carbohydrate bodies which, in great or less proportion, are convertible by treatment with a dilute mineral acid into sugars. It has also been observed that the sugar most constantly and abundantly yielded as the hydration product of those insoluble carbohydrates is galactose, indicating that the carbohydrate in most instances is paragalactin. Other carbohydrates appear to be contained in those seeds in addition to the galactose-yielding body, which has been shown by the optical and chemical properties of their inversion products. Further, the quantitative data obtained have enabled an approximately exact estimation to be made of the total sum of the nitrogen-free extract matters, and of the carbohydrate proportion of those matters which is directly convertible into sugars. In the example of Pisum sativum it was observed that one-fifth of the whole composition matter of the seed consisted of an insoluble carbohydrate which was almost wholly convertible into galactose. The nitrogen-free extract matter contained in the seeds of Phaseolus vulgaris did not amount to quite ten per cent. of the constituent substances; nearly the whole of that amount, however, as in the case of Pisum sativum, was convertible into galactose. The examples Faba vulgaris and Vicia sativa contained respectively about fourteen and fifteen per cent. of those non-nitrogenous bodies; but in those examples not more than one half of those amounts yielded to the action of the dilute mineral acid, giving sugar hydration products.

The main result achieved by these researches is the finding of a more intelligible and scientific expression for all that portion of the constituent matter of seeds hitherto practically considered as a non-nitrogenous, valueless residue, and indicating what may be

the function of those matters in the physiological economy of the plant. It also appears that those matters, constituting so large a part of seeds, may and do exercise a nutritive office in the animal system, which was also shown by the author in the artificial digestion studies of certain seeds.[1]

The question of the locality of those insoluble carbohydrates in the organism of the seed was studied microscopically by Prof. Cramer, Zürich, at the instance of Prof. E. Schulze. It appears that those bodies are secreted in the cells of the endosperm, and must be considered as a reserve material of the seed, and as contributing to the support of the embryo during germination. Prof. Cramer found in the examples of the cocoa palm, coffee, soja, and of the legume seeds specified in the researches, that the thick membranes of the cells of the cotyledons resist the direct action of a solution of cuprammonia; after, however, those membranes have been heated for a time in a dilute solution of mineral acid, whereby paragalactin and other carbohydrates are separated out, the cellulose residue of the membranes is soluble in the cupr. ammonia solution. Those membranes, before treatment with the acid, were insensible to color reagents. After the removal of the insoluble carbohydrates the cellulose residue gave a vivid blue reaction when treated with a mixture of chloride iodide of zinc.

Chemically, those insoluble carbohydrates are distinguished from the soluble carbohydrates and starch by their insolubility in water and diastase. From cellulose, as it has been shown, the distinction occurs in the solubility of those bodies in dilute acids and their non-solubility in cuprammonia, which is the reagent in which cellulose most readily dissolves.

HARVARD COLLEGE LABORATORY.

[1] This Journal **11**, No. 5.

REVIEWS AND REPORTS.

On the Formation of Ozone, Hydrogen Peroxide, and Nitrous Acid as Products of Combustion, and on their Presence in the Air.

It is hardly necessary to refer to the number of chemists who have already worked on this subject, or to commend the excellence of their work. The names of Schönbein, Houzeau, Schoene, Berthelot, and Traube will at once suggest themselves. It would seem, however, that they all worked under the same difficulty, the lack of proper reagents to distinguish accurately between the reactions of ozone, hydrogen superoxide, and nitrous acid. In recent numbers[1] of the *Bulletin de la Société chimique de Paris* there are six articles by Prof. L. Ilosvay de N. Ilosva, of the Polytechnic School at Buda-Pesth, which show very accurate and painstaking work, and, if the results obtained are reliable, will materially modify the ideas now held.

The first paper is on reactions of nitrous and nitric acids. The author finds in sulphanilic acid and napthylamine a reagent which acts on nitrous acid, but not on hydrogen peroxide or ozone. This reaction was discovered by Griess,[2] who first studied the action of diazo-benzene-sulphonic acid on napthylamine. He obtained his diazo-benzene-sulphonic acid by treating sulphanilic acid with nitrous acid, and calls attention to the extreme delicacy of the reaction, minute traces of nitrous acid sufficing to produce a dark red color in presence of dilute sulphuric acid. The colored substance formed is an amido-azo-derivative of the formula $C_6H_4(SO_3H)N=NC_{10}H_6NH_2$, called by Griess azo-amido-napthalene-benzene-sulphonic acid.

Ilosvay increases the sensitiveness of the reaction by substituting acetic for sulphuric acid. He can detect nitrous acid in aqueous solution in a dilution of one part of nitrous acid to one thousand million parts of water, but finds that quantitative determinations of nitrous acid cannot be made by this reagent. To detect nitric acid in the presence of nitrous, he first breaks down the latter by Peccini's[3] method with urea in the acidulated solution, and detects nitric acid by the blue color produced by diphenylamine and concentrated sulphuric acid. This is a fairly sensitive reaction, but its sensitiveness is limited to a dilution of $\frac{1}{950000}$, and it is caused by the oxidising agents as well as by nitric acid. For very dilute solutions it is better to reduce to nitrous acid and test by Griess's reaction. Granulated zinc in presence of alkali is the best reducing agent. In this way one part of nitric acid in two hundred and fifty million parts of water is easily detected.

[1] September and November, 1889. [2] Ber. d. chem. Gesell. **12**, 426; **15**, 2191.
[3] Ztschr. anal. Chem. 1880, 354.

The second paper is on the action of oxidising agents on azo-amido-napthalene-benzene-sulphonic acid, the coloring matter produced by Griess's reaction. Chlorine, dilute chromic acid, acidulated permanganate, and hydrogen peroxide turn this red substance orange yellow, the orange shade remaining when exposed to the air; and ozone turns the substance reddish yellow, changing on exposure to the air to a red shade, differing from the original red. These changes are supposed to be caused by the formation of oxy-azo compounds. From his experiments the author concludes that the amido-azo coloring substance can be used as a delicate reagent for ozone and hydrogen peroxide, and that nitrous acid can exist for a short time in the presence of ozone and hydrogen peroxide, because its oxidation is not immediate; but if enough ozone or hydrogen peroxide be present, it is quickly oxidised to nitric acid.

In the third paper, methods for preparing sodium hydroxide free from nitrous acid are described. This reagent is required for the following work, and is prepared either by decomposing water with sodium, or by reducing the nitrites contained in ordinary hydroxide with granulated zinc.

In the fourth article the author takes up the question of the formation of ozone, hydrogen peroxide, nitrous and nitric acids, as products of the active combustion of various substances and of the slow combustion of phosphorus. He reviews the literature and shows the divergence in the statements of the numerous chemists who have worked on this subject. He studies at length the various reagents, and commends as the best for ozone its odor, by which one can detect it in a dilution of $\frac{1}{1500000}$. The best chemical reagent is paper impregnated with thallium suboxide, which ozone turns brown, while hydrogen peroxide does not change it. It is true that nitrous acid turns it brown, but if the action continues, colorless thallium nitrate is formed. This is not as sensitive a test for ozone as its odor; the paper requires 20–25 minutes to turn brown with ozone in a dilution of $\frac{1}{1200000}$. The reagents commonly used to detect hydrogen peroxide are iodide of potassium and starch, chromic acid and ether, acidulated potassium permanganate, Wurster's[1] paper (impregnated with di- and tetra-methyl-phenylene-diamine), and titanium dioxide dissolved in concentrated sulphuric acid; the last mentioned is the only one not acted on by ozone or nitrous acid. Hydrogen peroxide turns it yellow. It is not very sensitive, but is a sure reagent to detect hydrogen peroxide in dilutions not exceeding $\frac{1}{900000}$.

It is to be noted that in a dilute solution hydrogen peroxide can exist in presence of an excess of ozone; but if it is in excess the ozone is destroyed. Hence both cannot be present unless ozone is in excess.

The author examined the products of combustion of hydrogen,

[1] Ber. d. chem. Gesell. **19**, 3208.

carbon monoxide, methane, illuminating gas, benzene, alcohol, ether, petroleum, stearin candles, magnesium, zinc, iron filings, sulphur, and phosphorus.

He examined the gases escaping from stoves heated with wood and with coke, the air surrounding the voltaic arc, and the products formed by the slow combustion of phosphorus. To test for ozone, the flames of the burning substances were covered with a glass tube, the gaseous products of combustion collected and tested with all reagents used for ozone. Thallium suboxide was not changed, and only those reagents which act on nitrous acid as well as on ozone were changed. In examining the slow combustion of phosphorus, the flask containing the phosphorus was filled with water and connected with two Peligot tubes filled with water; then followed a Winkler's absorption apparatus containing the amido-azo compound, then a tube with thallium suboxide paper, then an absorption tube with potassium iodide and starch, and finally an aspirator. The water in the flask was replaced by pure air (leaving a little water in contact with the phosphorus), and the aspirator set in motion; in four minutes after the phosphorus came in contact with air, the amido-azo compound turned yellow, one minute later the thallium protoxide turned brown, twelve minutes later the starch paste was quite blue. The water in the Peligot tubes gave no reaction for hydrogen peroxide, but it was found in the water in contact with the phosphorus. In the slow combustion of phosphorus, then, both ozone and hydrogen peroxide are formed.

Ilosvay then took up the question of the formation of hydrogen peroxide as a product of active combustion. He repeated the experiments of Traube,[1] and confirms Traube's statements that carbon monoxide does not burn in perfectly dry air, but burns in moist air, and that if the surface of water is brought in contact with the carbon monoxide flame, or with the hydrogen flame, the water will be found to contain hydrogen peroxide. But Ilosvay found that if carbon monoxide or hydrogen is burned in moist air and the product mixed with a little water, hydrogen peroxide is sometimes present, sometimes not; he discovered that its formation depends on the flame coming in contact with the moisture condensed on the sides of the vessel; that if the flame is small and kept in the centre of the vessel, avoiding contact with the walls, no hydrogen peroxide is formed. These results led him to try whether all combustible gases and vapors when burned in contact with water form hydrogen peroxide. He burned carbon monoxide, hydrogen, methane, illuminating gas, alcohol, ether, petroleum, stearin candles, and benzene in a suitable apparatus, directing the flames into water. As a result, the water was found in every case to contain hydrogen peroxide after a minute or two.

Ilosvay says: "Considering that ozone is decomposed at 240°, and hydrogen peroxide at dull red heat, it is not supposable that

[1] Ber. d. chem. Ges. **18**, 1891.

either could exist in a hot flame, and not surprising that hydrogen peroxide was only formed when the flame was cooled by contact with water."

He burned all the above-mentioned substances in air, and mixed the products of combustion with water, and in no case was the water found to contain hydrogen peroxide. He passed the products of combustion of fuel through water, and proved that no hydrogen peroxide was formed. Nitrous and nitric acids were always formed by quick combustion of the substances mentioned, and were best absorbed by dilute alkali (a 20 per cent. solution of pure sodium hydroxide). He attributes the formation of acids of nitrogen to the union of nitrogen and oxygen of the air, brought about by the heat of combustion of the substances burned.

To see whether the higher oxides of nitrogen are formed in the flameless combustion of solids, he heated, both in pure air and in oxygen, in a suitable tube, magnesium, zinc, and iron reduced by hydrogen; both nitrous and nitric acid are formed in all cases. Ilosvay wishes to experiment further before expressing an opinion whether in these cases the formation depends on the temperature or not.

One might suppose that on uniting in a eudiometer dry hydrogen and dry oxygen in presence of an excess of oxygen, hydrogen peroxide could be formed as a secondary product, and that ozone might be formed when carbon monoxide unites with oxygen in presence of an excess of oxygen. The author purified and dried these gases, introduced them into eudiometers over dry mercury, and exploded them. No matter in what proportions the gases were mixed, no hydrogen peroxide nor ozone was formed, but in all cases *nitrous* and *nitric* acids. He says that of course his gases must have contained traces of air, the nitrogen of which was oxidised. The difficulty of getting gases absolutely free from air is known to chemists, and Ilosvay thinks it extremely difficult, if not impossible, to remove the last traces of air, as in these experiments he worked with every known refinement and precaution. The author asks whether the oxides of nitrogen are not a more important constituent of the air and of vegetable growth than now supposed, whether reactions attributed to ozone and hydrogen peroxide are not caused entirely or in part by nitrous acid.

The fifth paper answers the question, Does the air contain ozone or hydrogen peroxide? Ozone is supposed to be formed by active and slow combustion, by electric discharges in the air, and in the evaporation of water. It is supposed that in slow combustion hydrogen peroxide is also formed. The author has not succeeded in finding ozone among the products of active combustion, nor on the evaporation of water. In passing an electric spark through air ozone is not formed, but he finds nitrous acid, thus confirming the observations of Cavendish and those of Böttger.[1]

[1] Jahresbericht, 1858, 102.

Slow combustion, as in the decay of vegetable matter, cannot form ozone, because if it did we should find most ozone near the soil. Hartley and Scontellen[1] have shown that it is not found there. By the action of a Holtz electric machine ozone and the higher oxides of nitrogen are both formed, and the author thinks it probable that if ozone is formed in the air it must be by silent electric discharges.

Ilosvay bases his tests on the results of two previous experiments:

1. Hydrogen peroxide oxidises alkali nitrite to nitrate, and if present in excess can be recognised by titanic acid.

2. Ozonised air passed through a 20 per cent. solution of sulphuric acid and a 4 per cent. solution of sodium hydroxide reacts quickly with the amido-azo compound, with thallium suboxide and with potassium iodide.

The apparatus used consisted of:

1. A Winkler absorption tube with 20 per cent. NaOH;
2. A Pettenkofer tube 550 cm. long containing 20 per cent. H_2SO_4;
3. A Pettenkofer tube a meter long containing 4 per cent. sodium hydroxide;
4. A small Peligot tube with 4 per cent. sodium hydroxide;
5. A Winkler absorption tube containing a dilute solution of amido-azo color;
6. A small empty Peligot tube;
7. A Winkler tube containing potassium iodide;
8. A straight tube containing protoxide of thallium paper, and Wurster's tetra-methyl-phenylene-diamine paper;
9. A small Peligot tube containing strong sodium hydroxide;
10. A straight tube with Lender's ozonometer;
11. A washing bottle with soda;
12. A gas meter;
13. A water pump.

All the apparatus and connections were of glass and constructed with such care that when the whole system was connected it held a column of mercury 534 mm. high for several hours. The parts containing reagents were protected from the light by black cloths; the air was pumped from outside the window of the laboratory. The first experiment lasted fifteen days and nights. 774,244 liters of air were drawn through the apparatus. The second experiment lasted five days and nights, and 500 liters of air were drawn through the apparatus. The result of these trials was that no ozone was detected. In the first Winkler tube nitrous and nitric acids and traces of ammonia were found; in the sulphuric acid tube a little ammonia; in the Pettenkofer tube, containing 4 per cent. sodium hydroxide, very little nitrous and nitric acids and still less ammonia; in the small Peligot tube filled with sodium

[1] Fehling, Handwörterbuch **4**, 1087.

hydroxide minute traces of these three compounds. The first three tubes were examined for hydrogen peroxide, but none was found.

These experiments were made in May and June; the weather was fine with frequent thunder-storms, and was such as is supposed to be favorable to the formation of ozone and hydrogen peroxide.

Single tests made on mountains, in the country and in the city, under varied conditions of weather, confirm these results. The author says that he finds more nitrous acid in the air in spring than in the autumn; more in the day-time than at night; and that the amount increases with the height of the layers of air. He wishes this paper to be considered preliminary.

In his sixth paper he confirms Schönbein's statement that saliva contains nitrous acid, and Struve's statement that the air exhaled from the lungs contains ammonium nitrite, and he also shows that the air exhaled by animals contains more nitrous acid than ordinary air.

In the November number of the *Bulletin*, Ilosvay has a short article on the presence of nitrous acid in the air. Grass and the leaves of trees cut in the morning while covered with dew were washed with pure water; the water then gave the reaction for nitrous acid. Grass cut at noon and in the evening yielded no nitrous acid, unless the day had been cloudy without rain. Nitric acid and ammonia were always found, no matter when the grass was cut. These results were confirmed by numerous experiments, and Ilosvay concludes that either nitrites or nitrates are always present on the surface of plants; but that in dry clear weather nitrites are oxidised to nitrates either by oxygen escaping from the pores of the leaves or by oxygen of the air aided by the action of the sun's rays.

Specimens of sand, sandy soil and loam containing much humus were washed until free from oxides of nitrogen, carefully dried and exposed to the air. At the end of twelve hours all the specimens gave the reactions for nitrous and nitric acids and ammonia. In a parallel series of experiments, air freed of oxides of nitrogen was conducted over specimens of the dried soils, and no nitrites, nitrates, nor ammonia were formed. This shows that the soil takes up nitrous and nitric acids and ammonia directly from the air, and suggests that the nitrites and nitrates contained in the air, whatever their source, help to furnish the nitrogen necessary for plant life.

In the *Bulletin* of Dec. 5th, 1889, Ilosvay gives the details of several additional interesting experiments. Böttger[1] has affirmed that the oxygen made by the action of concentrated sulphuric acid on potassium permanganate contains ozone. Leeds[2] on the other hand maintains that ozone is not formed in this reaction, and that the reactions ascribed by Böttger to ozone were due to chlorine

[1] Jahresbericht, 1862, 44. [2] Chemical News **39**, 18.

contained in the permanganate. Ilosvay treated dry permanganate with concentrated sulphuric acid. Both reagents were shown to contain no chlorine; the oxygen generated was passed through three absorption tubes containing respectively water, a solution of the amido azo-dye, and a dilute solution of potassium iodide and starch paste. The violet-colored gas passed through the water, coloring it rose; it turned the dye yellow, and set iodine free. No chlorine being present, these reactions suggested ozone; but the author found that a dilute aqueous solution of pure potassium permanganate, as well as free chlorine or ozone, turns the azo-dye yellow, and sets free the iodine of a perfectly neutral or slightly acidulated solution of potassium iodide. This led him to suppose that the oxidising action in the above experiment might be due to permanganic anhydride, Mn_2O_7. By repeating the experiment, passing the oxygen first through two wash-bottles so as completely to absorb all permanganic anhydride, he found that neither the azo-dye, the potassium iodide, nor thallium oxide paper is affected by the oxygen; but if this precaution is not taken, one can obtain every reaction by which ozone is characterised; *i. e.*, in addition to those mentioned, the bleaching of indigo solution, the production of silver peroxide on metallic silver, the oxidation of lead hydroxide to lead peroxide, and that of lead sulphide to lead sulphate. The author therefore concludes that the reactions attributed to ozone in the action of sulphuric acid on permanganate may be due to chlorine if the permanganate contains chlorine, but that, otherwise, they are due to permanganic anhydride, and that no ozone is formed.

The author then examined the oxygen produced by the action of concentrated sulphuric acid on potassium dichromate, and found the characteristic ozone reactions; but shows that they are caused by chlorine contained in the dichromate. After so modifying his apparatus as completely to absorb the chlorine, the oxygen passed for an hour and a half over the reagents without acting on them.

Led by observations which showed that at high temperatures nitrogen has much affinity for hydrogen, oxygen, and carbon, forming ammonia, nitrous and nitric acids, and cyanogen, the author conducted pure air over heated platinum in the form of foil, of sponge, and of platinum black. In each of these forms platinum has the property of causing the union of nitrogen with oxygen at comparatively low temperatures, forming nitrous acid, as proved by the usual reagents. No ozone is formed. With platinum foil the action takes place between 280° and 350°; but, after heating an hour and a half, the platinum loses the property of causing union of nitrogen and oxygen. With platinum black the action commenced at 180°, was most marked at 250°, and diminished rapidly above 300°. With platinum sponge action began at 250°, was strongest at 300°, and diminished above 350°. After use, both the black and sponge lose the power of causing action. After some time, however, all kinds of platinum regain the power.

To test the ease with which nitrogen unites with oxygen, the author reduced ferric oxide to iron, by heating it in a tube in a current of hydrogen at a temperature not above 350°. After it had cooled in a current of hydrogen he heated it in the same tube in a current of dry pure air. At 190° the iron commenced to absorb some of the air passing over it. This absorption continued up to 250°. The air passing over the iron was conducted through a solution of pure sodium hydroxide. After heating for an hour, the sodium hydroxide was shown to contain minute traces of nitrous acid, but the iron oxide formed in the tube when treated with water gave a strong reaction for nitrous acid. That the iron oxide contains either nitrates or nitrites of iron is shown by again reducing it in a current of hydrogen, when aqueous vapor and ammonia escape with the hydrogen.

The author notes that iron reduced by hydrogen does not become incandescent in a current of dry air, even at a temperature of 400°; but in contact with moist air it becomes incandescent at 100°. Consequently the quick oxidation of iron depends not only on the fine division of the metal and the temperature at which it has been reduced, but also on the moisture in the air.

E. Renouf.

Allotropic Forms of Silver.

The May number of this Journal contains an abstract of M. Carey Lea's first article on the Allotropic Forms of Silver. He has since published three supplementary articles,[1] giving the results of his further work on the subject. Since writing his first paper he has spent much time in determining definitely whether the solubility of his first allotropic form *A* is due to a combination of the silver with citric acid.

"Many attempts were made to get a decisive indication, and two series of analyses, one a long one, to determine the ratio between the silver and the citric acid present, without obtaining a wholly satisfactory result, inasmuch as even these determinations of mere ratio involved a certain degree of previous purification which might have caused a separation.

"This question has since been settled in an extremely simple way, and the fact established that the soluble blue substance contains not a trace of combined citric acid.

"The precipitated lilac-blue substance (obtained by reducing silver citrate by ferrous citrate) was thrown on a filter and cleared of mother-water as far as possible with a filter pump. Pure water was then poured on in successive portions until more than half the substance was dissolved. The residue, evidently quite unchanged, was of course tolerably free from mother-water. It was found that by evaporating it to dryness over a water-bath most of the

[1] Am. Jour. of Sci. **38**, 47, 129, 237.

silver separated out as bright white normal silver; by adding water and evaporating a second time, the separation was complete, and water added dissolved no silver. *The solution thus obtained was neutral.* It must have been acid had any citric acid been combined originally with the silver. This experiment, repeated with every precaution, seems conclusive. The ferrous solution used for reducing the silver citrate had been brought to exact neutrality with sodium hydroxide. After the reduction had been effected, the mother-water over the lilac-blue precipitate was neutral or faintly acid.

"A corroborating indication is the following. The portions of the lilac-blue substance which were dissolved on the filter (see above) were received into a dilute solution of magnesium sulphate, which throws down insoluble allotropic silver of the form I have called *B* (see previous paper). This form has already been shown to be nearly pure silver. The magnesia solution, neutral before use, was also neutral after it had effected the precipitation, indicating that no citric acid had been set free in the precipitation of the silver.

"It seems therefore clear that the lilac-blue substance contains no combined citric acid. Had the solubility of the silver been due to combination with either acid or alkali, the liquid from which it was separated by digestion at or below 100° C. must have been acid or alkaline; it could not have been neutral.

"We have therefore this alternative. In the lilac-blue substance we have either pure silver in a soluble form, or else a compound of silver with a perfectly neutral substance generated from citric acid in the reaction which leads to the formation of the lilac-blue substance."

The later papers add several interesting points in reference to the properties of allotropic silver.

"The three forms of allotropic silver which were described in the June number of this journal—the blue soluble and the blue and the yellow insoluble—are not to be understood as the only forms which exist, but as the best marked only. The substance is protean and exhibits other modifications not yet studied. No other metal than silver appears to be capable of assuming such a remarkable variety of appearances. Every color is represented. I have obtained metallic silver blue, green (many shades of both), red, yellow, and purple. In enumerating these colors I do not refer to interference colors produced superficially by reagents, also wonderfully brilliant, but to body colors. As a single instance of coloration, the following may be mentioned: I recently obtained a solution of allotropic silver of an intense yellow brown. A little solution of disodic phosphate changed this to bright scarlet (like Biberich scarlet), presently decolorising with formation of a purple precipitate. Washed on a filter this changed to bluish green. The colors I have met with in this investigation can only

be compared with the coal-tar products, of which one is constantly reminded by their vividness and intense colorific power."

It is found that the superficial color reactions, mentioned in the first paper, can be obtained by other reagents than the halogen compounds there mentioned.

"Paper brushed over with either the gold, the copper-colored, or the bluish green substance exposed to the vapor of *ammonium sulphide*, or immersed in a dilute solution of it, assumes beautiful hues, though less brilliant than those obtained in some other ways.

"Potassium permanganate in dilute solution produces blue, red, and green colors.

"Potassium ferricyanide in moderately strong solution gradually attacks allotropic silver, with production of splendid blue, purple, and green coloration.

"Phosphorous acid produces gradually a rather dull coloration.

"The color reaction is produced finely by substances which readily part with a halogen, such as ferric and cupric chlorides, sodium hypochlorite, hydrochloric acid to which potassium bichromate has been added, and by corresponding bromine and iodine compounds. . . .

"The perchlorides of platinum, gold, and tin do not give the color reaction, though by analogy one would expect that they should, since they can lose chlorine with formation of a lower chloride."

When the silver is in a pure condition the alkaline haloids do not give the color reaction, as was at first supposed.

"The two insoluble forms of allotropic silver, described as *B* and *C*; *B*, bluish green, *C*, rich golden color—show the following curious reaction. A film of *B*, spread on glass and heated in a water stove to 100° C. for a few minutes, becomes superficially bright yellow. A similar film of the gold-colored substance *C* treated in the same way acquires a blue bloom. In both cases it is the surface only that changes."

All the forms of allotropic silver are sensitive to light. *A* when exposed to the sunlight soon becomes brown. The bright blue-green variety of *B* is changed into the pure gold-colored variety of *C*. Other forms of *B* turn brown on exposure to light.

The red-yellow variety of *C* changes to bright gold color. "Continued exposure seems to produce little further change so long as the substance is dry. But if the paper on which the silver is extended is kept moist by a wet pad, with three or four days of good sunshine, the change goes on until the silver becomes perfectly white, is apparently changed to normal silver: water, alone, tends to darken this form of allotropic silver, accordingly the portion of the paper that was protected for comparison darkened, showing that the whitening effect was due wholly to light. . . .

"The white silver thus obtained has all the character of ordinary silver and does not show the color reaction with ferric and cupric chloride, potassium ferricyanide, etc. Just in proportion to the exposure to light, the ability to give the color reaction diminishes, so that after a day's exposure, when the exposed part has become bright yellow, the color reagents scarcely affect this yellow, whilst the protected part becomes intense blue, purple or green. In this way it is easy to observe the gradual effect of light as it changes the allotropic silver, finally converting it into what resembles in every way, and is undoubtedly, ordinary silver."

The specific gravity of the forms *B* and *C* was found by careful determinations to be less than that of normal silver. *B* = 9.58, *C* = 8.51, normal silver = 10.5, or 10.62 when in the condition of a finely divided precipitate.

In reference to physical condition the author says: "The brittleness of the substances *B* and *C*, the facility with which they can be reduced to the finest powder, makes a striking point of difference between allotropic and normal silver. It is probable that normal silver, precipitated in fine powder and set aside moist to dry gradually, may cohere into brittle lumps, but these would be mere aggregations of discontinuous material. With allotropic silver the case is very different, the particles dry in optical contact with each other, the surfaces are brilliant and the material evidently continuous. That this should be brittle indicates a totally different state of molecular constitution from that of normal silver. . . .

"When gold-colored allotropic silver is gently heated in a test-tube it undergoes a remarkable change in cohesion. Before heating it is brittle and easily reduced to fine powder. After heating it has greatly increased in toughness and cannot be pulverised at all."

Both the insoluble forms *B* and *C* resemble normal silver in disengaging oxygen from hydrogen dioxide.

All the forms are much more sensitive to light than ordinary silver.

W. V. METCALF.

NOTES.

Absorption of Nitrogen during Slow Oxidation.

In the August (1889) number of the *Annales de Chimie et de Physique*, M. Berthelot gives the results of some experiments upon the absorption of nitrogen during processes of slow oxidation, as in the case of the soil and of plants. It has been found

that certain substances, as, for example, ether, turpentine, certain aldehydes, oleic acid, etc., possess the power of absorbing free oxygen, and when brought into contact with some substance capable of easy oxidation, again yielding it up in such way as to bring about this oxidation. Thus potassium iodide is oxidised by treating it with ether which has stood a long time in contact with air. If pure water be shaken with such ether, it will act, after separation from the ether, like a solution of hydrogen peroxide when brought into the presence of chromates. According to M. Berthelot, by exposure to the air ether becomes converted into an oxidation product, $C_8H_{20}O_8$, and this decomposes in the presence of water:

$$C_8H_{20}O_8 + H_2O = 2C_4H_{10}O + H_2O_2.$$

If ether which has stood in contact with the air a long time be treated with lime-water absolutely free from nitrates, the aqueous solution on evaporation yields a residue which with ferrous sulphate and strong sulphuric acid reveals the presence of nitric acid. If carefully purified ether be allowed to stand in contact with pure water or with pure lime-water for a considerable length of time, a trace of nitric acid is formed. Passage of air, bubble by bubble, through pure ether produces the same result. Ether can thus convert a minute portion of the nitrogen of the air into nitric acid. In the case of turpentine the detection of the nitric acid is difficult, since strong sulphuric acid acts upon the aqueous solution of the products of the oxidation of the turpentine, forming an intense yellow color which masks that due to nitric acid. M. Berthelot comes to the conclusion that, in the case of turpentine, mesitylene, benzoic aldehyde, and oleic acid, if the formation of nitric acid does take place, the quantity is no greater than in the case of ether. Experiments undertaken to discover whether ammonia is formed in the oxidation of iron by means of pure water gave no positive results; the fact that the iron used often contains a trace of combined nitrogen prevents the experimenter from coming to any definite conclusion with regard to the matter.

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